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A STUDY OF RAPID SOLIDIFICATION

OF HYDROCARBON FUELS

FINAL REPORT

BY

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This research effort was carried out under Contract DA 44-177-TC-819 by the Southwest Research Institute, and was aimed at finding means by which aircraft fuels can be rapidly gelled in an effort to decrease damage and loss of life due to post-crash fires.

The report has been reviewed by the U. S. Army Transportation Research Command and is considered to be technically sound.

The conclusions made by the contractor are considered by this Command to be valid.

A STUDY OF RAPID SOLIDIFICATION OF HYDROCARBON FUELS

Final Report

Prepared by

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for
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FORT EUSTIS, VIRGINIA

ABSTRACT

Progress is reported on rapid methods for gelling aircraft fuels. The most promising systems consist of amines and diisocyanates. The properties of the gel are influenced by the structure of the amine and isocyanate. Various types of gels can be produced. These include particulate, viscoelastic, and dilatant gels. Gelation rates as fast as 0.04 second were obtained. In addition, several systems will rapidly gel fuel from -55°C to 60°C. The results show that the various gels will retard the burning rate of the fuels and will contain the fuel while burning. The viscoelastic and dilatant gels have excellent impact properties. The gelation of aircraft fuel will significantly decrease the fuel vaporization rate. A comparison was made of the various gels prepared. Some of the gels are almost as effective at 2.5 weight percent concentration as at a concentration of 4.0 weight percent.

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SUMMARY

This research program was concerned with the investigation of various techniques by which hydrocarbon fuels may be rapidly solidified. The purpose of this investigation was to develop a gelling system that will rapidly gel aircraft fuel and prevent fuel misting if the fuel tank is ruptured in a plane crash.

Previous experience has shown that two chemical systems appeared promising for the rapid solidification of hydrocarbon fuels. One involved the reaction of dibasic acid chlorides with amines to form amides or polyamides. The second system consisted of reacting isocyanates with amines. Both systems have extremely fast reaction rates and were considered worthy of investigation.

With respect to the investigation of the polyamide system, several dibasic acid chlorides and amines were synthesized and evaluated by reacting them in the presence of JP-4. The compiled data indicate that when a specific primary monoamine is reacted with various dibasic acid chlorides, the results obtained with respect to the gelation of JP-4 are essentially the same. In all of the experiments, an excess of the amine was used in order to remove the HCl formed.

In view of the aforementioned observations, a series of tests were made in which various amines were dissolved in JP-4 and hydrogen chloride gas was bubbled into the solution. In all instances, the same type of gel or precipitate was obtained with the amines as was obtained when the amines were reacted with various dibasic acid chlorides. Thus the data show that the gels that were obtained were due to the formation of the amine hydrochloride and not the amide or polyamide formation.

The major effort during this program involved the reaction of isocyanates and amines to produce substituted ureas. Early in the program, experiments showed that the rate of gelation and the type of gel obtained depended on the structure of both the amine and the isocyanate.

Several gelling systems were developed that will rapidly gel JP-4. The rates of gelation ranged from several minutes to as fast as 0.04 second. It was of interest to note that the majority of the more

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rapid gelling systems involved the use of certain aromatic diisocyanates and either an aliphatic amine or an alkoxyamine.

Various types of gels were also prepared by varying the structure of the amine or isocyanate. For example, an aliphatic diisocyanate such as hexamethylene diisocyanate and an alkoxyamine (2-ethylhexyl-3-aminopropyl ether) converts JP-4 into a tough visco-elastic gel. This gel has excellent impact properties in that it contains the fuel under impact conditions.

Numerous systems were also developed that will convert JP-4 into a particulate type of gel. This type of gel was obtained with aliphatic, aromatic and alicyclic amines, or diamines, as well as the corresponding isocyanates and diisocyanates. In general, the systems producing the particulate gels had fast rates of gelation and good burning properties in that there was little or no flow of the gel while burning.

The use of aromatic triisocyanates and aliphatic amines or alkoxyamines converted JP-4 into a tough dilatant gel. An example of this system is 2, 4, 6-toluene triisocyanate and 2-ethylhexyl-3-aminopropyl ether. This gel had excellent burning properties in that it significantly decreased the rate of burning and showed no tendency to flow. The disadvantage of this system is that the triisocyanate is a solid and only slightly soluble in JP-4 at room temperature.

It was desirable to prepare a fuel gel that would retard the burning rate and would not melt while burning. During this program various gelling systems were designed that would not melt while burning and would retard the burning rate. Some of the gels burned as long as 15 to 16 minutes and did not melt. Under the same conditions an equal weight of JP-4 burned in approximately 1. 0 minute. The particulate type of gels displayed the best burning properties. It was also of interest to note that those gels prepared from compounds containing a high percentage of aromatic rings as well as halogen substituted aromatic rings significantly retarded the burning rate. Typical additives are the β - ethoxyethylamine-4, 6-dimethyl-1, 3-xylylene diisocyanate system and the 4-chlorobenzylamine-m-xylylene diisocyanate system.

Some information was also obtained concerning the vaporization rate of gelled JP-4 as compared to liquid JP-4. With liquid JP-4, an

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air velocity of 20 liters/minute was required to reduce the hydrocarbon vapors below the explosive limits. One of the best systems was 4-chlorobenzylamine and 4, 6-dimethyl-1, 3-xylylene diisocyanate. These additives at a total concentration of 4. 0 weight percent retarded the vaporization rate to the point where 2. 5 liters of air/minute was enough to decrease the hydrocarbon concentration below the explosive limits.

A series of tests were made in an effort to evaluate the various gelling systems. Of the numerous systems compared, some have fast gelation rates, some have excellent burning properties (retarded burning rate), and some have good impact properties in that they contain the fuel under impact conditions. Examination of the results shows that several of the additive systems received excellent ratings in two or more of the tests; however, no additive system was developed that excelled in all of the evaluation tests. The results obtained from these experiments do show a trend and indicate the types of structures that should produce the optimum gel.

CONCLUSIONS

Various amines and dibasic acid chlorides were evaluated during the course of this program. With the compounds used and the conditions under which they were evaluated, it is concluded that the gels obtained were produced by the formation of the amine hydrochloride and not by amide or polyamide formation.

The major effort during this program was spent in the synthesis and evaluation of amines and isocyanates. It was found that the structure of both the amine and the isocyanate influence the rate of gelation, the burning rate, the vaporization rate, the gel rigidity, and the properties of the gel under impact conditions.

Several gelling systems were developed that have extremely fast rates, the fastest being 0.04 second. The structure of the reactants significantly influenced the rate of gelation. For example, with a specific amine, the rate of gelation was faster using 4, 6-dimethyl-1, 3-xylylene diisocyanate than it was using m-xylylene diisocyanate. The rate of gelation was also influenced by the structure of the amine. With the same diisocyanate, dodecenyl-2-aminoethyl ether had a faster gelation rate than did 2-ethylhexyl-3-aminopropyl ether.

During the course of this investigation, various types of gels were prepared. Some of the gels were particulate, others visco-elastic, and some displayed dilatancy.

The particulate gels were normally obtained using aromatic diisocyanates with aromatic or aliphatic amines. The general properties of this type of gel were the good gelation rates and good burning properties in that the burning rate was significantly retarded. In addition, they contained the fuel while burning, as they did not melt or flow. The majority of the additive systems producing particulate gels functioned over a wide temperature range; however, at the maximum ranges (-55°C to 60°C), many of the systems lost some of the gel strength and the gelation rate was retarded. Regarding the impact properties, these gels did contain a high percentage of the fuel; however, some was lost in the impact test. The gel that was thrown from the container remained in lumps and did not form a mist.

The viscoelastic type of gel was usually obtained when either the isocyanate or the amine contained an ether linkage. The best viscoelastic gels were prepared using aliphatic diisocyanates and alkoxyamines. This class of compounds rapidly gelled the fuel and functioned exceptionally well over the entire temperature range investigated. They significantly retarded the fuel vaporization rate and displayed excellent impact properties. These gels contained all of the fuel when subjected to an impact force of 580 G's. They did have poor burning properties in that once ignited they melted and flowed over a wide area.

The dilatant gels were obtained using aromatic triisocyanates and certain aliphatic or alkoxyamines. These gels displayed interesting properties in that they could be shaped or molded. If not contained, they had a tendency to flow; however, when subjected to shear they became quite rigid, and under impact conditions they would "bounce like a rubber ball". If one considers the impact properties, burning properties, gel strength, and effect on fuel vaporization rate, the dilatant gels are the best gels prepared to date. The disadvantage of this system is that the aromatic triisocyanates evaluated during this program are relatively insoluble solids and as such cannot be rapidly injected into the fuel.

Various tests were made to evaluate the gels with respect to the rate of gelation, burning properties, vaporization rate, gel rigidity, and performance under impact conditions. F amination of the results shows that several of the additive systems performed exceptionally well in two or more of the tests; however, no additive system was developed that excelled in all of the evaluation tests.

The results indicate that the system which will rapidly gel the fuel, produce a gel that will contain the fuel under impact conditions and while burning, and retard the burning rate is a trifunctional amine and/or isocyanate containing both aromatic rings and ether linkages.

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RECOMMENDATIONS

It is recommended that the investigation of ureas as gelling agents for aircraft fuels be continued. Evaluation of the results obtained definitely indicates that the optimum gelling system will consist of a trifunctional amine and/or isocyanate containing both aromatic rings and ether linkages.

With respect to the triisocyanates, those evaluated during this program were solids and, as a result, would not function in the rapid gelation of fuels. However, the possibility exists that separation of the isocyanate group from the aromatic ring by a methylene or ethylene group will produce a liquid triisocyanate having a much greater reaction rate. This trend was observed with diisocyanates. For example, m-phenylene diisocyanate is a liquid, but the gelation rate was slow when reacted with an amine in JP-4. p-xylylene diisocyanate is a solid. m-xylylene diisocyanate is a liquid having a rapid reaction rate with amines in JP-4. In the above proposed triisocyanate, the groups will be meta to each other and separated from the ring by a methylene group. This compound should contain the favorable properties of the individual diisocyanates. The proposed compound is listed below.

where n is 1 or 2 and R can be H or an alkyl group. This compound can be reacted with alkoxy amines or aromatic amines containing halogen groups or alkoxy groups. This combination would produce a gellant high in aromatic rings, ether groups and a triurea linkage.

Another type of triisocyanate worthy of investigation is one containing both ether linkages and an aromatic ring. Experiments using 2-ethylhexyl-3-aminopropyl ether and dodecenyl-2-aminoethyl ether with various diisocyanates have shown that the presence of the ether linkage significantly lowers the melting point of the amine. It also increases the temperature range at which rapid gelation will occur and improves the impact properties.

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Two general formulas are listed below.

$$OCN-(CH_2)_n-O-\underset{I}{\overset{R}{\bigcirc}}\begin{array}{l} -O-(CH_2)_n-NCO \\ O-(CH_2)_n-NCO \end{array}$$

$$OCN-(CH_2-CH_2-O)_n-\underset{II}{\overset{R}{\bigcirc}}\begin{array}{l} -(O-CH_2-CH_2)_n-NCO \\ (O-CH_2-CH_2)_n-NCO \end{array}$$

In compound I, n is 1 to 4 and R is H or an alkyl group. Some of the precursors for synthesizing this type of compound have been prepared.

With compound II, n is 1 through 4 and R is H or an alkyl group. With this type of compound it is known that the presence of the alkoxy group significantly lowers the melting point. This general type of alkoxy linkage is present in many liquid nonionic surfactants having much higher molecular weights than proposed here.

The general type of triisocyanates discussed above can be reacted with alkoxyamines, aromatic amines, or halogen containing amines to produce a gelling agent high in ether linkages, aromatic rings, and with a triurea linkage.

The second proposed approach to the liquid triisocyanate is to prepare an aliphatic triisocyanate containing ether linkages. It is believed that this type of triisocyanate will undoubtedly be a liquid having a low melting point. The presence of the ether linkage will increase the reaction rate, and the low melting point will increase the temperature range over which gelation will occur.

This type of compound can be obtained from aliphatic triols or trihalides. Two examples of the types of compounds proposed are listed on the following page. For the purpose of illustration, trimethylol propane is used as the aliphatic trisubstituted starting material.

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$$O-(CH_2)_n-NCO$$
$$|$$
$$CH_2$$
$$|$$
$$CH_3-CH_2-C-CH_2-O\,(CH_2)_n-NCO$$
$$|$$
$$CH_2$$
$$|$$
$$O-(CH_2)_n-NCO$$

III

$$(O-CH_2-CH_2)_n-NCO$$
$$|$$
$$CH_2$$
$$|$$
$$CH_3-CH_2-C-CH_2\,(-O-CH_2-CH_2)_n-NCO$$
$$|$$
$$CH_2$$
$$|$$
$$(O-CH_2-CH_2)_n-NCO$$

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In compound III, n is 1 to 4; in compound IV, n is from 1 to 6. These aliphatic ether-containing compounds can be evaluated with various aromatic amines or halogen substituted aromatic amines.

One significant advantage of the proposed synthesis of triisocyanates is that similar triamines can be synthesized by the same process. Since the same conditions are involved in the synthesis of amines, the combination of synthesized additives should yield the optimum fuel gelation system as indicated by the results obtained during this program.

INTRODUCTION

The objective of this program was to investigate various chemical systems that will rapidly gel hydrocarbon fuels. The purpose of such an investigation is to rapidly gel aircraft fuel immediately prior to an impending crash. Gelation of the fuel will prevent spillage and eliminate misting of the fuel.

As reported previously, * a rapid fuel gelling system was developed. This system involved the reaction of lauryl amine with the various isomers of tolylene diisocyanate.

This program was concerned with the development of an additive system that will rapidly gel the fuel, contain the fuel under impact conditions, retard the rate of vaporization, retard the burning rate or flammability of the gel, and contain the fuel while burning. Tests were designed to evaluate the aforementioned properties. In addition, a literature search was made on the gelation of hydrocarbons.

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* A Study of Rapid Solidification of Hydrocarbon Fuels, TRECOM Technical Report 63-50, prepared by Southwest Research Institute for U.S. Army Transportation Research Command, Fort Eustis, Virginia, October 1963.

DISCUSSION

Previous experiments have shown that the most promising systems for investigation are the polyamides and the ureas. These systems will form gels that fall into three general classifications. They are particulate gels, viscoelastic gels, and dilatant gels. The general discription of a particulate gel is one that will form a rigid structure; however, when placed under shear, the gel structure is broken and will not reform when the force is removed. Viscoelastic gels are elastic when placed under stress, and when the stress is removed, they have a tendency to return to their original shape. Dilatant gels show a rapid viscosity increase under stress, and under a rapid application of force, as occurs in a plane crash, the viscosity increase is so great that the gel performs as a solid.

AMIDES AND POLYAMIDES AS GELLING AGENTS

Previous experiments have shown that amides and polyamides are promising gelling agents for jet fuels. The reaction between an acid chloride and an amine is extremely rapid and should be applicable to the problem of rapidly gelling JP-4.

To initiate this study, a series of experiments were made in which adipyl chloride was reacted with various amines in the presence of JP-4. The results of these tests are listed in Table 1. Of the various amines investigated, it may be observed that the resulting amides failed to gel the fuel.

In Table 2, a series of amines were reacted with sebacoyl chloride in JP-4. In run number 5-39-4, 1.5 weight percent sebacoyl chloride and 1.5 weight percent Alamine 21D (coco amine) converted JP-4 into a viscoelastic gel. The gel was inferior to that obtained with the amine-diisocyanate system but it does indicate the feasibility of the amide system.

The aforementioned experiments and various amide systems previously reported (TRECOM Technical Report 63-50) have shown that, in general, the polyamides made from commercially available dibasic acid chlorides have a tendency to precipitate from JP-4. This is to be expected since these materials were developed for the purpose of preparing insoluble high-molecular-weight polymers. As a result, experiments were designed to build into the polymer a degree of hydrocarbon solubility. To accomplish this, several dibasic acid chlorides

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were synthesized via the malonic ester synthesis. The general reactions are listed below:

1.
$$
\begin{array}{c}
\text{COOEt} \\
| \\
\text{CH}_2 \\
| \\
\text{COOEt}
\end{array}
\quad + \quad \text{Na} \longrightarrow
\begin{array}{c}
\text{COOEt} \\
| \\
\text{Na-CH} \\
| \\
\text{COOEt}
\end{array}
$$

2.
$$
\text{R-Cl} \quad + \quad
\begin{array}{c}
\text{COOEt} \\
| \\
\text{Na-CH} \\
| \\
\text{COOEt}
\end{array}
\longrightarrow
\begin{array}{c}
\text{COOEt} \\
| \\
\text{R-CH} \\
| \\
\text{COOEt}
\end{array}
$$

The product from reaction 2 was hydrolyzed to the corresponding dibasic acid and then converted to the dibasic acid chloride.

3.
$$
\begin{array}{c}
\text{COOEt} \\
| \\
\text{R-CH} \\
| \\
\text{COOEt}
\end{array}
\quad + \quad \xrightarrow[\text{H+}]{\text{HOH}}
\begin{array}{c}
\text{COOH} \\
| \\
\text{R-CH} \\
| \\
\text{COOH}
\end{array}
$$

4.
$$
\begin{array}{c}
\text{COOH} \\
| \\
\text{R-CH} \\
| \\
\text{COOH}
\end{array}
\quad + \quad \text{PCl}_5 \longrightarrow
\begin{array}{c}
\text{COCl} \\
| \\
\text{R-CH} \\
| \\
\text{COCl}
\end{array}
$$

The first two dibasic acid chlorides synthesized were octyl malonyl chloride and dodecyl malonyl chloride. Analysis of the octyl malonyl chloride showed the product to be essentially pure (Chlorine analysis: Theoretical 28.0%; Found, 27.5%). The dodecyl malonyl chloride did contain some impurities (Chlorine analysis: Theoretical ?3.0%; Found 19.0%). Infrared analysis showed the presence of a small amount of free acid. The possibility exists that a small amount of decarboxylation also occurred in the "three-step" synthesis.

With respect to evaluating these dibasic acid chlorides, Table 3 lists the results obtained from the reaction of dodecyl malonyl chloride with various amines in the presence of JP-4. In run number 5-47-1, dodecyl malonyl chloride was reacted with Alamine 21D (coco amine). The product converted JP-4 to a viscoelastic gel which improved on standing. It might be noted that in run number 5-39-4 as listed in Table 2, when sebacoyl chloride was reacted with the same amine, the reaction product also produced a viscoelastic gel. However, this gel was somewhat firmer than the one obtained using dodecyl malonyl chloride. With the other runs listed in Table 3, the product was either soluble in JP-4 or formed a flocculent precipitate.

Table 4 lists the results obtained from the reaction of octyl malonyl chloride with various amines in the presence of JP-4. In run number 6-6-2, coco amine (Alamine 21D) was reacted with octyl malonyl chloride to produce a viscoelastic gel. The rigidity of this gel increased somewhat with time. It may also be observed that when unsaturated primary monoamines such as tall oil amine, oleyl amine, and cotton-seed oil amine were reacted with octyl malonyl chloride, the product was soluble in JP-4. With respect to the diamines, it might be noted that when dodecyl malonyl chloride was reacted with dimer diamine, the product formed a flocculent or particulate precipitate; but when octyl malonyl chloride was used, the product formed a sticky semisolid which agglomerated into a wax-like mass.

In attempting to analyze the results obtained by reacting various amines with the octyl malonyl chloride and dodecyl malonyl chloride, it was of interest to note that when both dibasic acid chlorides were reacted with the same primary monoamines, similar results were obtained. These results were compared with previously reported results obtained with the same amine and other dibasic acid chlorides (Table 2, and Table 2 of the Interim Report dated October 1963). It might be noted that several runs in the Interim Report were repeated. This was done in order to compile previous screening tests and have all pertinent information immediately available so that this system can be fully evaluated.

In analyzing the results obtained with specific amines, it was surprisingly noted that similar results were obtained even though the structures of the aliphatic dibasic acid chlorides were quite different. For example, using Alamine 4D (lauryl amine) as the specific amine with adipyl chloride (run number 5-38-2, Table 1), the product formed a thin slurry; and with sebacoyl chloride (run number 5-39-6, Table 2), a dense slurry of voluminous solids was obtained. With the same amine, dodecyl malonyl chloride and octyl malonyl chloride (Tables 3 and 4) formed similar products.

In an effort to elucidate the aforementioned phenomena, a series of tests were made in which dodecyl malonyl chloride was reacted with a mixture of primary and tertiary amines. Since the tertiary amines are in general stronger bases than the primary fatty amines, it was thought that they would selectively react with the HCl. The results of these tests are listed in Table 5. In run number 6-24-1, dodecyl malonyl chloride was reacted with a mixture of coco amine and pyridine in JP-4. The resultant viscoelastic gel was similar to the one obtained using only dodecyl malonyl chloride and coco amine.

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When tributyl amine was used as the tertiary amine (run number 6-25-5), the viscoelastic gel obtained was similar to the one obtained when the tributyl amine was omitted.

In the two preceding experiments, the results indicate that the presence of the tertiary amine had little or no influence on the property of the resultant gel. However, in run number 6-25-6, n-methyl morpholine was mixed with coco amine and the mixture was then reacted with dodecyl malonyl chloride in JP-4. Using this tertiary amine, no gel was obtained.

In run number 6-25-8, tributyl amine was added to JP-4. When dodecyl malonyl chloride is added to this mixture, a suspension of solids is obtained. This indicates that some free HCl is present in the dibasic acid chloride. However, when coco amine is added, a viscoelastic gel is formed.

When n-methyl morpholine and dodecyl malonyl chloride is added to JP-4, a fine precipitate is obtained (run number 6-25-9). If coco amine is added to this mixture, the precipitate dissolves but no gel is obtained.

PHOSPHORUS-CONTAINING DIBASIC ACID CHLORIDES AND AMINES AS GELLING AGENTS

While investigating various dibasic acid chlorides and amines as gelling agents for JP-4, a simultaneous program was conducted in which phosphorus-containing dibasic acid chlorides were evaluated by reacting them with various amines in JP-4. These materials were investigated in an effort to build some fire retardation properties into the gel.

The first dibasic acid chloride of phosphorus evaluated was phenyl dichlorophosphate. This compound was reacted with various amines in the presence of JP-4. The results of these tests are listed in Table 6. In run number 6-10-1, the phenyl dichlorophosphate was reacted with lauryl amine, and the product produced a fine precipitate which slowly settled. With coco amine (run number 6-10-2), a weak viscoelastic gel was obtained.

In Table 7, p-tolyl dichlorophosphate was reacted with the same amines. The products obtained with respect to gelation of JP-4 were essentially the same as was obtained with the phenyl dichlorophosphate.

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It was most interesting to note that, as shown in Table 8, when chloromethyl phosphonic dichloride and the same amines were reacted, the results were essentially identical to those obtained with the other phosphorus containing dibasic acid chlorides even though the structures are quite different.

The compiled data indicate that when a specific primary mono-amine is reacted with various dibasic acid chlorides, the results obtained with respect to the gelation of JP-4 are essentially the same. This observation has been made with a number of amines and various dibasic acid chlorides. In all of these experiments an excess of the amine was used in order to remove the HCl formed.

In view of the aforementioned observations, a series of tests were made in which various amines were dissolved in JP-4 and hydrogen chloride gas was bubbled into the solution. In all instances, the same type of gel or precipitate was obtained with the amines as was obtained when the specific amines were reacted with various dibasic acid chlorides. Thus, these data show that the gels that were obtained were due to the formation of the amine hydrochloride and not to amide or polyamide formation.

UREAS AND POLYUREAS AS GELLING AGENTS

During the first year's contract on fuel gelation, experiments showed that JP-4 can be rapidly gelled using diisocyanates and amines as reactants. The most promising system consisted of tolylene diiso-cyanate and a fatty amine such as lauryl amine. These addit.ves formed a particulate type of gel. The rate of reaction was fast, but the resultant gel was not as strong as desired.

During this program a large number of mono- and diamines as well as mono- and diisocyanates were synthesized and evaluated. These compounds were synthesized in an effort to improve the rate of gelation, increase the gel rigidity, and decrease the burning rate. It is known that the presence of halogens on a polymeric chain will retard the rate of burning. In order to determine the flame-retarding effectiveness of halogen atoms in a gelled fuel, experiments were initiated to prepare 1-chloro-2, 4-benzene diisocyanate. Due to the unavailability of the diamine derivative, it was necessary to start with 1-chloro-2, 4-dinitrobenzene.

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This compound was reduced to the corresponding diamine and isolated as the dihydrochloride. Some difficulty was encountered in this separation. The dihydrochloride was then converted to the corresponding diisocyanate by phosgenation. Preliminary experiments made while attempting to isolate the diisocyanate indicated that this material did not have the expected reactivity. Infrared analysis showed this material to contain some 1-chloro-2, 4-dinitrobenzene. This experiment was repeated in order to obtain a pure product. After the 1-chloro-2, 4-dinitrobenzene was reduced, it was isolated as the free amine. This eliminated the solubility problem encountered with the diamine dihydrochloride. The compound was analyzed by determining the percent NCO present (theory, 48.0%; found 42.8%). The results of the evaluation are listed in Table 9. In run number 6-8-1, the diisocyanate was reacted with lauryl amine in the presence of JP-4. Immediately after the two reactants were mixed, the product appeared to be soluble; but after approximately 0.5 hour, the product precipitated from the fuel. This phenomenon had not been observed before. It was not believed that the rate of reaction was that slow because with other amines listed in Table 9, the diisocyanate reacted immediately and precipitated from the solution.

If the results listed in Table 9 are compared with the results obtained by reacting various amines with other aromatic diisocyanates (Interim Report, October 1963), it is noted that the presence of the chlorine group on the aromatic ring increases the solubility of the resultant polyurea in JP-4.

In addition to halo-containing aromatic diisocyanates, aliphatic diisocyanates were synthesized in order to determine the types of gels they will produce. The first aliphatic diisocyanate investigated was decamethylene diisocyanate. This compound was prepared by phosgenating decamethylene diamine dihydrochloride. The results of the evaluation tests are listed in Table 10. In run number 5-49-1, Alamine 21D (coco amine) was reacted with decamethylene diisocyanate in JP-4. This system gelled JP-4, but the rate of gelation was slower than was obtained with tolylene diisocyanate and the same amine. In addition, the gel obtained from the decamethylene diisocyanate and coco amine was granular and the fuel separated on standing. In run number 5-49-2, lauryl amine and decamethylene diisocyanate produced a firmer gel than did the above-mentioned system, but the fuel again separated on standing.

In an effort to increase the solubility of the resultant polyurea in JP-4, Formonyte 608 (oleyl amine manufactured by Foremost Chemical Products Company) was reacted with decamethylene diisocyanate. A good gel which did not separate on standing was obtained. However, the gel is not as rigid as the one obtained from Hylene TM-65 and lauryl amine.

In view of the results obtained with decamethylene diisocyanate and unsaturated fatty amines, a series of tests were made in which hexamethylene diisocyanate was reacted with various amines in JP-4. The results of these tests are listed in Table 11. In run number 6-2-1, oleyl amine (Formonyte 608) was reacted with hexamethylene diisocyanate in the presence of JP-4. The product formed a firm gel. With respect to gel rigidity, this gel is superior to the one obtained using Hylene TM-65 and lauryl amine.

Tetramethylene diisocyanate was likewise synthesized and evaluated by reacting it with various amines in JP-4. The results of these tests are listed in Table 12. In run number 6-26-1, tetramethylene diisocyanate and oleyl amine rapidly formed a gel when reacted in JP-4. However, this gel was not as firm as was obtained using hexamethylene diisocyanate. When hexyl amine was reacted with tetramethylene diisocyanate as shown in run number 6-26-3, the reaction was so fast that good mixing could not be obtained. As a result, a higher concentration of additives was present near the surface of the fuel. A rigid gel was obtained; however, in a few minutes the fuel exuded from the gel.

As the various diisocyanates were evaluated, a simultaneous program was carried out in which various amines were evaluated. Previous results had shown that the type of gel obtained as well as the rate of gelation is greatly influenced by the structure of both the amine and the isocyanate.

In order to determine what effect an ether linkage has on the gel, 2-ethylhexyl-3-aminopropyl ether (Amine 803) was evaluated by reacting it with various diisocyanates in JP-4. The results of these tests are listed in Table 13. In run number 6-27-1, Amine 803 was reacted with Hylene TM-65. The product formed a thick gel that appeared to have some viscoelastic properties. However, this gel was inferior to the one obtained using lauryl amine and Hylene TM-65. In run number 6-27-2,

Amine 803 was reacted with hexamethylene diisocyanate. The product is a tough viscoelastic gel. It was of interest to note that this same diisocyanate when reacted with oleyl amine produced a good rigid particulate gel. In run number 6-27-3, the total concentration of additives was decreased to 2.0 weight percent. The resulting visco-elastic gel was slightly weaker than that obtained at the 4.0 weight percent level. At the 1.0 weight percent level, the gel obtained is too weak for the intended use.

When Amine 803 was reacted with tetramethylene diisocyanate (run number 6-31-4 as listed in Table 12), a viscoelastic gel was ob-tained. The gel was inferior to the one obtained using hexamethylene diisocyanate and the same amine. A mixture of Amine 803 and hexyl amine when reacted with tetramethylene diisocyanate formed a firm gel and did not display any viscoelasticity. However, this gel was inferior to the one obtained with hexamethylene diisocyanate and oleyl amine.

Since the 2-ethylhexyl-3-aminopropyl ether when reacted with aliphatic diisocyanates in JP-4 forms viscoelastic gels which should display good properties under impact conditions, an ether-containing aromatic diisocyanate was synthesized and evaluated. This ether-containing diisocyanate, 4-methoxy-m-phenylene diisocyanate, was synthesized by phosgenation of the corresponding diamine dihydro-chloride. This compound is a solid having a melting point of 73-74°C (literature reported a mp of 75°C). This material was evaluated by reacting it with various amines in the presence of JP-4. The results of these tests are listed in Table 14. Because of its low solubility in JP-4, it was necessary to heat the fuel. It is realized that this insolubility eliminates 4-methoxy-m-phenylene diisocyanate as a potential fuel gellant; however, these tests were made in order to determine the effect of the methoxy group. It can be noted that with both coco amine and 2-ethylhexyl-3-aminopropyl ether, tough visco-elastic gels were obtained. However, due to the insolubility of the diisocyanate and the slow rates of gelation, no further work was done.

During the early phase of this program, two triisocyanates were synthesized. These were 1,3,5-benzene triisocyanate and 2,4,6-toluene triisocyanate. Since these materials are solids, they were not evaluated immediately because they cannot be rapidly injected in JP-4. However, it was decided to evaluate these compounds in order to determine if the product of these trifunctional materials and amines will gel fuel.

The first triisocyanate to be reacted with various amines was 1, 3, 5-benzene triisocyanate. The results of these tests are listed in Table 15. It was noticed that the triisocyanate is practically insoluble in JP-4. It was necessary to heat the fuel to around 65°C in order to partially dissolve the triisocyanate. In run number 6-35-1 when the 2-ethylhexyl-3-aminopropyl ether was added, it reacted with the partially dissolved triisocyanate. In about one hour all of the triisocyanate had dissolved and reacted to form a tough viscoelastic gel. On cooling, a good dilatant gel was obtained.

In view of the insolubility of benzene triisocyanate in JP-4, an attempt was made to prepare a concentrated solution of the triisocyanate and then inject this solution into JP-4. Numerous solvents were tested, but none was found that would dissolve the triisocyanate. Since the compound was originally crystallized from hexane, it is believed that the triisocyanate had dimerized.

While the benzene triisocyanate was being evaluated, similar tests were being conducted with 2, 4, 6-toluene triisocyanate. The results of these tests are listed in Table 16. The toluene triisocyanate was also insoluble in JP-4. However, to evaluate this system, the JP-4 was heated to approximately 65°C in order to partially dissolve the triisocyanate. In run number 6-36-1, 2-ethylhexyl-3-aminopropyl ether was added to the hot JP-4 triisocyanate system. In approximately 5 minutes, all of the triisocyanate had dissolved and reacted. The product converted the fuel to a very tough gel. On cooling, a dilatant gel was obtained. This was undoubtedly the best gel obtained to date. This gel, containing a total additive concentration of 4.2 weight percent, could be shaped or molded. If not contained, the gel had a tendency to flow like an extremely viscous solution; however, on impact it would "bounce like a rubber ball".

Because of the insolubility of this triisocyanate, various solvents were screened in an effort to prepare a concentrated solution. No solvent was found. The possibility exists that the 2, 4, 6-toluene triisocyanate had dimerized. When the triisocyanate was synthesized, it had a melting point of 74° to 76°C (literature reports a mp of 75°C). The material used in the evaluation tests started melting at 140°C and had not completely melted at 210°C. This indicates that the material had dimerized.

In view of the excellent gels obtained with the dimers of 1, 3, 5-benzene triisocyanate and 2, 4, 6-toluene triisocyanate, the monomers were again synthesized. The first to be synthesized was 2, 4, 6-toluene triisocyanate. One of the difficulties with this material is that it is a solid and dissolves slowly in the JP-4. In order to evaluate this material, it was melted before addition to the fuel. The results of these tests are listed in Table 17. In run number 7-7-1, the triisocyanate was reacted with 2-ethylhexylamine. This system rapidly gelled the fuel. The gel was dilatant and one of the best prepared during this program. With coco amine a similar gel was obtained. It was of interest to note that the gel obtained using 2-ethylhexyl-3-amino-propyl ether (Amine 803) was not as rigid as was obtained using coco amine or 2-ethylhexyl amine. When the Amine 803 was reacted with the dimer of 2, 4, 6-toluene triisocyanate (Table 16, run number 6-36-1) a more rigid gel was obtained.

It is necessary that the fuel additives are liquids so that they can be rapidly injected into the fuel. Two of the best solvents obtained to date are hexamethylene diisocyanate and toluene diisocyanate. Using these two diisocyanates, solutions containing 50 weight percent 2, 4, 6-toluene triisocyanate can be prepared providing that the temperature of the solution is maintained at 30°C or above. These solutions, each containing 50 weight percent 2, 4, 6-toluene triisocyanate, were evaluated by reaction with various amines in JP-4. The results of these tests are listed in Table 18. In run number 7-10-1, the hexamethylene diisocyanate (HDI) 2, 4, 6-toluene triisocyanate (TTI) mixture was reacted with 2-ethylhexylamine. This system slowly thickened the fuel; after approximately 1 minute it formed a dilatant gel. It is of interest to note that when only HDI is reacted with the same amine, it slowly forms a precipitate (run number 7-6-2 in Table 30), and TTI with the same amine (run number 7-7-1 in Table 17) rapidly converts the fuel to a dilatant gel. If one analyzes the data as listed in Table 18, it can be noted that similar results were obtained with the isocyanate solution consisting of 50 weight percent Hylene TM-65 and 50 weight percent 2, 4, 6-toluene triisocyanate.

The results obtained in the evaluation of 1, 3, 5-benzene triisocyanate are listed in Table 19. Of the various tests run, it can be noted that the rate of reaction was entirely too slow. In addition, 1, 3, 5-benzene triisocyanate is a solid. In order to rapidly inject the triisocyanate into the fuel, it would be necessary to keep the triisocyanate in a molten state or have it available as a solution. Neither would be

feasible, since in the molten state the triisocyanate will slowly dimerize; if it is in solution, the solvent would be present as excess weight. In view of this, no further work was done using the 1, 3, 5-benzene triisocyanate.

During the course of this program, numerous aromatic diisocyanates were synthesized and evaluated as gelling agents. With respect to gelation rate, several diisocyanates reacted extremely fast with certain amines to produce particulate types of gels. These gels displayed good burning properties in that they did not melt while burning and retarded the rate of burning when compared to similar gels prepared from aliphatic diisocyanates and amines.

One of the diisocyanates evaluated was p-xylylene diisocyanate. This diisocyanate is a solid melting at 42° to 44° C. The compound was prepared by reacting 1, 4-bis(bromomethyl) benzene with silver cyanate. This diisocyanate was reacted with various amines in the presence of JP-4. The results of these tests are listed in Table 20. In run number 7-19-1, a precipitate was obtained when p-xylylene diisocyanate was reacted with coco amine in JP-4. When oleyl amine (run number 7-19-2) was reacted with p-xylylene diisocyanate, the product gelled the JP-4; however, the gel was soft and easily broken. In run number 7-19-6, p-xylylene diisocyanate was reacted with 2-ethylhexyl-3-aminopropyl ether (Amine 803) in JP-4. The rate of reaction was too fast to obtain good mixing. The product formed a tough viscoelastic gel. Burning and impact tests were made on this gel and will be discussed in the Evaluation section.

m-Phenylene diisocyanate was also evaluated by reacting it with various amines in JP-4. The diisocyanate was prepared by phosgenation of the corresponding diamine dihydrochloride. In run number 7-23-1, as listed in Table 21, m-phenylene diisocyanate when reacted with oleyl amine required approximately two minutes to convert JP-4 into a weak thixotropic gel. It was of interest to note that this same diisocyanate when reacted with lauryl amine and coco amine immediately formed a weak, grainy, particulate gel.

In run number 7-23-5, m-phenylene diisocyanate was reacted with Amine 803 (2-ethylhexyl-3-aminopropyl ether) in JP-4. This system required approximately 10 minutes before it formed a tough viscoelastic gel. The runs listed in Table 21 show that the rate of reaction of m-phenylene diisocyanate with primary amines is too slow for the gelation of aircraft fuels.

In the rapid gelation of jet fuels, one important criterion is that the additives are liquids so that they can be rapidly injected into the fuel. The p-xylylene diisocyanate, as discussed above, was a solid. The literature revealed that m-xylylene diisocyanate is a liquid. In view of this, the m-isomer was synthesized by phosgenating the corresponding diamine dihydrochloride. In run number 7-50-1, as listed in Table 22, the m-xylylene diisocyanate-4-chlorobenzyl amine system instantaneously formed a very firm particulate gel. Some free fuel was observed; however, it is thought that this was due to inadequate mixing.

In run number 8-1-1, the above system was evaluated using a total additive concentration of 1.0 weight percent. The gel was about as firm as when a total of 4.0 weight percent additives was used.

When m-xylylene diisocyanate was reacted with p-phenetidine (run number 8-6-1), a very dry particulate gel was obtained in approximately 1.0 minute. o-Phenetidine and the same diisocyanate formed a precipitate (run number 8-6-4).

In an effort to investigate the influence of alkyl groups on the aromatic diisocyanate, 4,6-dimethyl-1,3-xylylene diisocyanate was synthesized and evaluated by reaction with amines in JP-4. In run number 8-28-1, as listed in Table 23, 4,6-dimethyl-1,3-xylylene diisocyanate was reacted with 4-chlorobenzylamine in JP-4 and instantaneously formed a dry particulate gel. This gel had a greater cohesive strength than did the gel obtained with the same amine and m-xylylene diisocyanate. When 4-isopropylbenzylamine and 4,6-dimethyl-1,3-xylylene diisocyanate were reacted in JP-4, they instantaneously formed a dry particulate gel that could be readily crumbled.

In run number 8-29-4, p-phenetidine when reacted with 4,6-dimethyl-1,3-xylylene diisocyanate rapidly formed a dry particulate gel. This same amine when reacted with m-xylylene diisocyanate required more than 1.0 minute to gel the fuel (run number 8-6-1, Table 22).

When 4,6-dimethyl-1,3-xylylene diisocyanate was reacted with n-hexylamine (run number 8-31-3), the rate of reaction was too fast to obtain good mixing. By dissolving each reactant in half of the fuel and then rapidly pouring the two solutions into a third container, it was possible to obtain a good particulate gel. However, when the same diisocyanate was reacted with 2-ethylhexylamine the rate of gelation was much slower. In addition, it formed a weak viscoelastic gel.

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By comparing the results obtained with 4, 6-dimethyl-1, 3-xylylene diisocyanate and m-xylylene diisocyanate, it can be noted that the presence of the methyl groups significantly increased the rate of gelation when reacted with various amines.

Several alicyclic diisocyanates were prepared in order to obtain some information concerning the influence of this type of structure on the rate of fuel gelation as well as the types of gels produced by the presence of the alicyclic groups.

One alicyclic diisocyanate screened was 1, 4-bis(isocyanatomethyl) cyclohexane. This diisocyanate was prepared by phosgenating 1, 4-bis(aminomethyl) cyclohexane dihydrochloride. This diisocyanate was evaluated as a fuel gelling agent by reaction with various amines in JP-4. The results of these tests are listed in Table 24. In run number 7-24-3, the above-mentioned diisocyanate was reacted with oleyl amine in JP-4. The reaction product formed a weak grainy gel which was easily broken. With Amine 803 this same diisocyanate required approximately 3 minutes to convert the fuel to a tough viscoelastic gel. The other amines tested either formed a very weak particulate gel or precipitates in JP-4.

Another alicyclic diisocyanate evaluated was menthane diisocyanate. This compound was synthesized by phosgenating the corresponding diamine dihydrochloride. Table 25 lists the results obtained when menthane diisocyanate was reacted with various amines in the presence of JP-4. If one examines the results, it may be noted that several systems gelled the fuel. These gels were too weak to warrant further investigation. Furthermore, the rate of reaction was too slow to apply to the problem concerned.

In addition to the aromatic diisocyanates, alicyclic diisocyanates, and aliphatic diisocyanates that were screened during this program, several monoisocyanates were also evaluated. These included an aryl isocyanate and an aliphatic isocyanate.

In an effort to obtain information concerning the rate of reaction with respect to the gelation of JP-4, oleyl isocyanate was reacted with various amines. The oleyl isocyanate was prepared by phosgenation of oleyl amine. In run number 7-35-2 as listed in Table 26, 1, 4-bis(aminomethyl) cyclohexane was reacted with oleyl isocyanate to form a weak grainy gel. When 1, 4-bis(isocyanatomethyl), cyclohexane was reacted

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with oleyl amine (run number 7-24-3, Table 24), it formed a weak grainy gel. With respect to the overall properties of both systems, they were essentially the same. This was to be expected since the major product is the same in both experiments. However, one would expect some difference in the rate of gelation especially with respect to the isocyanate group. This was found to be true in that the rate of gelation of the 1, 4-bis(aminomethyl) cyclohexane-oleyl amine system. This same observation was made with the menthane diamine-oleyl isocyanate system and the menthane diisocyanate-oleyl amine system. These runs are listed as 7-35-1 and 7-31-1 respectively. In both examples cited above, the oleyl isocyanate-alicyclic diamine systems were the fastest.

One of the aromatic monoisocyanates investigated was 3-chlorophenyl isocyanate. The results of these tests are listed in Table 27. When reacted with unsaturated fatty amines, the 3-chlorophenyl adducts are soluble in the fuel. Soluble products were also obtained when 3-chlorophenyl isocyanate was reacted with n-hexyl amine, 2-ethylhexyl amine, t-octyl amine, and Amine 803.

In run number 7-43-1, 2.2 weight percent of 3-chlorophenyl isocyanate was reacted with 1.8 weight percent of 4-chlorobenzyl amine to instantaneously form a very firm, dry particulate gel. The rate of gelation is so fast that the only way good mixing could be obtained was to divide the fuel into two beakers, add one additive to each half of the fuel, and then rapidly pour the solutions into a third beaker.

In run number 7-46-4, the concentration of the reactants was decreased from 4 weight percent to 2 weight percent. At the lower concentration, the gel obtained was equivalent to the one obtained at the 4 weight percent level.

Another aromatic isocyanate screened during this program was α-naphthyl isocyanate. Table 28 lists the results obtained when α-naphthyl isocyanate was reacted with various amines in JP-4. In run number 8-38-1, α-naphthyl isocyanate and lauryl amine were used as the reactants. It is estimated that this system required approximately 5 seconds to form a firm particulate gel. It was of interest to note that oleyl amine (run number 8-38-4) and tall oil amine (run number 8-38-5) when reacted with the same isocyanate formed products that were soluble in jet fuel. However, when the isocyanate was reacted with coco amine, which also contains a high percentage of unsaturation, the reaction product formed a good particulate gel.

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While screening the various types of isocyanates and diisocyanates by reacting them with various amines, it was quite evident that the structure of the amine or diamine significantly influenced the rate of fuel gelation as well as the type of gel produced. In view of this, several amines and diamines were screened in order to elucidate the observed phenomena.

The first of the amines evaluated with the exception of the fatty amines was t-octyl amine (1, 1, 3, 3-tetramethyl butylamine). The results of these tests are listed in Table 29. In run number 6-48-2, t-octyl amine was reacted with Hylene TM-65 (65 percent 2, 4-toluene diisocyanate and 35 percent of the 2, 6-isomer) in the presence of JP-4. This system formed a gel similar to the one obtained with Hylene TM-65 and lauryl amine; however, the rate of gelation was slower.

In run number 7-9-2, 2, 6-tolylene diisocyanate was reacted with t-octyl amine. In approximately 1 minute, this system formed a precipitate in JP-4. Using 2, 4-tolylene diisocyanate with the same amine formed a product soluble in JP-4. In these runs the rate of reaction was slow indicating that the two methyl groups on the number 1 carbon were blocking the amine group.

The results obtained using the t-octyl amine and the various isomers of toluene diisocyanate shows that the structure of the diisocyanate significantly influences the solvation of the product in the JP-4. On surveying the results obtained, one can note that the product obtained with 2, 4-tolylene diisocyanate and t-octyl amine is soluble in JP-4. Using the 2, 6-isomer and the same amine will produce a precipitate in JP-4. When a mixture of the two isomers is reacted with the same amine, a rigid particulate gel is obtained. In all cases the rate of reaction was slow.

In run number 7-9-3, 2, 4, 6-toluene triisocyanate and t-octyl amine formed a precipitate in JP-4. It was necessary to melt the triisocyanate in order to obtain rapid dissolution when added to the jet fuel.

The second aliphatic amine tested was 2-ethylhexyl amine. When this amine was reacted with Hylene TM-65 (run number 7-6-1 as listed in Table 30) in JP-4, approximately two minutes was required to convert the fuel to a weak gel. When hexamethylene diisocyanate and 2-ethylhexyl amine were reacted in JP-4, the product rapidly

precipitated from the fuel. This same amine and 2,6-tolylene diiso-
cyanate rapidly formed a dispersion of gelatinous solid.

In comparing the results obtained (Tables 29 and 30) with the
various amines and tolylene diisocyanates, it is apparent that the rate
of reaction as well as the product formed with respect to the gelation
of JP-4 is dependent on the structure of both the diisocyanate and the
amine.

Included with the aliphatic amines was a N,N-dialkyl-diamine.
The amine was diethylaminopropylamine.

The results of these tests are listed in Table 31. In run number
8-35-1, Hylene TM-65 was reacted with the above amine in JP-4. The
system immediately formed a thick suspension of solids that displayed
some thixotropic properties. Similar results were obtained when m-
xylylene diisocyanate was reacted with the same amine (run number 8-
36-1).

In run number 8-36-2, hexamethylene diisocyanate was reacted
with diethylaminopropylamine and immediately converted JP-4 to a dry
particulate gel. This gel was similar to the other dry particulate gels
in that it had very little cohesive strength. The other isocyanates when
reacted with diethylaminopropylamine either formed precipitates or
were soluble in the fuel.

A long chain diamine containing an aromatic ring was synthesized
and evaluated. This diamine, N,N-bis(aminobutyl) benzylamine, was
synthesized according to the following equations:

5.
$$\langle\underset{=}{\bigcirc}\rangle\text{-}CH_2Cl \; + \; HN\text{-}(CH_2\text{-}CH_2\text{-}CH_2\text{-}CN)_2 \longrightarrow$$

$$\langle\underset{=}{\bigcirc}\rangle\text{-}CH_2\text{-}N\text{-}(CH_2\text{-}CH_2\text{-}CH_2\text{-}CN)_2$$

6.
$$\langle\underset{=}{\bigcirc}\rangle\text{-}CH_2\text{-}N\text{-}(CH_2\text{-}CH_2\text{-}CH_2\text{-}CN)_2 \xrightarrow{\text{LiAlH}_4}$$

$$\langle\underset{=}{\bigcirc}\rangle\text{-}CH_2\text{-}N\text{-}(CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2)_2$$

The diamine was evaluated by reaction with various diisocyanates in the presence of JP-4. The results of these tests are listed in Table 32. It may be noted that the isocyanates or diisocyanates when reacted with N, N-bis(aminobutyl)benzylamine formed precipitates in JP-4. The possibility exists that if the aryl group is substituted with a branched alkyl group, the solubility would be increased. This would tend to form a gel in JP-4 in place of a precipitate.

Several alicyclic amines, heterocyclic amines, and aromatic amines were evaluated in order to determine the types of fuel gels that can be obtained when these materials are reacted with isocyanates or diisocyanates in JP-4.

Typical alicyclic amines that were screened as potential gelling agents when reacted with isocyanates and diisocyanates are cyclohexylamine and 1, 4-bis(aminomethyl) cyclohexane. With respect to the evaluation of cyclohexylamine, the results of these tests are listed in Table 33. In run number 7-37-1, cyclohexylamine was reacted with Hylene TM-65 in JP-4. This system rapidly formed a thick suspension of solids. When cyclohexylamine was reacted with hexamethylene diisocyanate (run number 7-37-3), it converted the fuel to a very weak gel. The other diisocyanates tested formed precipitates in JP-4.

Table 34 lists the screening tests made in the evaluation of 1, 4-bis(aminomethyl)cyclohexane and various isocyanates. It can be observed that the reaction products formed precipitates in every test made.

An example of a heterocyclic amine was 3-aminomethyl pyridine. The results of these tests are listed in Table 35. In run number 7-44-2, 3-aminomethyl pyridine and Hylene TM-65 formed a dense suspension of solids in JP-4. The rate of reaction was extremely fast. With the other 3-aminomethyl pyridine-diisocyanate systems investigated, the rates of reaction were extremely fast and precipitates were obtained in all cases.

When JP-4 was gelled with an aromatic triisocyanate and amines containing an aromatic ring, the resultant gels had excellent burning properties in that the rate of burning was slow and the gels remained rigid and did not flow. In view of this, various aromatic amines and substituted aromatic amines were evaluated in an effort to obtain a system that will, when reacted with an isocyanate or diisocyanate, rapidly convert JP-4 to a rigid gel having good impact and burning properties.

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The simplest of the aromatic amines evaluated was aniline. In run number 8-8-1 as listed in Table 36, aniline was reacted with m-tolyl isocyanate in JP-4. The rate of gelation was too slow in that it required approximately 5 minutes to form a very dry particulate gel. The same amine when reacted with p-tolyl isocyanate forms a precipitate. With all of the isocyanates or diisocyanates tested, the rate of gelation was too slow to apply to the rapid gelation of hydrocarbon fuels.

Similar results were also obtained when o-toluidine was evaluated by reaction with isocyanates or diisocyanates in JP-4. The results of these tests are listed in Table 37. In run number 7-49-1, o-toluidine was reacted with m-xylylene diisocyanate in JP-4. This system required several minutes to completely gel the fuel. The gel was dry and very hard. It was a particulate type of gel and could be readily crumbled into small pieces. However, as with aniline, when o-toluidine was reacted with isocyanates or diisocyanates, the rate of reaction was too slow to apply to the rapid gelation of JP-4.

Previous experiments have shown that firm dry particulate gels can be obtained by reacting aromatic diisocyanates with aromatic amines. These gels are very firm; however, they have little cohesive strength. In an effort to increase the cohesive strength of the gels, various substituted aromatic amines were synthesized and screened.

Table 38 lists the results obtained when 4-chlorobenzylamine was reacted with diisocyanates. This amine should affect the burning rate of the gel since it contains a halogen. In run number 8-3-4, 4-chlorobenzylamine and Hylene TM-65 instantaneously reacted to form a weak grainy gel. The rate of reaction was so fast that good mixing could not be obtained. Hexamethylene diisocyanate and 4-chlorobenzylamine likewise produced a weak grainy gel. The rate of reaction was very fast; however, it was not as rapid as the 4-chlorobenzylamine-Hylene TM-65 system.

In order to increase the chlorine content of the gelling system, several attempts were made to gel JP-4 using 2,4-dichlorobenzylamine and various diisocyanates. The results of these tests are listed in Table 39. If one examines the results obtained, it can be noted that with all of the systems tested, only precipitates were obtained.

In order to obtain a product that will gel JP-4, it is necessary to design the reactants so that when reacted the product has a structure

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which displays the proper solubility in the fuel. If the solubility is not great enough, a precipitate is obtained; if it is too great, the product is soluble in JP-4. In the evaluation tests for chlorobenzylamines, weak gels or precipitates were obtained. The aforementioned screening tests also showed that with the same diisocyanate, the rate of gelation is much faster with benzylamine or a substituted benzylamine than is the rate with aniline or a substituted aniline.

One technique to increase the solubility of the urea in JP-4 is to use an alkylated benzylamine. Such a compound is 4-isopropyl-benzylamine. This compound was reacted with various diisocyanates in JP-4. The results of these tests are listed in Table 40. In run number 8-16-2, 4-isopropylbenzylamine was reacted with m-xylylene diisocyanate in JP-4. This system rapidly converted the fuel to a dry particulate gel. The gel had little cohesive strength and would readily crumble. A similar type of gel was obtained when hexamethylene diiso-cyanate was reacted with the same amine (run number 8-17-1).

In run number 8-16-4, menthane diisocyanate was reacted with 4-isopropylbenzylamine to form a product soluble in JP-4. This was interesting, since in previous screening tests using menthane diiso-cyanate and various aromatic amines, only precipitates were obtained. These results show that a larger alkyl group is needed on the benzene ring of the amine in order to obtain the desired solubility. The solu-bility can also be enhanced by incorporating an alkoxy group on the benzene ring of the amine or on the ring of the aromatic diisocyanate.

Previous experiments with ?-ethylhexyl-3-aminopropyl ether (Table 13) showed that the presence of the ether group significantly influenced the properties of the gel. The gels obtained with this amine were viscoelastic and had excellent properties under impact conditions.

In view of the above findings, several additional alkoxyamines were synthesized.

The first alkoxyamine to be synthesized was dodecenyl-2-amino-ethyl ether. The amine was synthesized by reacting dodecenyl chloride (1-chloro-5, 5, 7, 7-tetramethyl-2-octene) with the sodium salt of ethanolamine. The general reaction is shown as follows:

7. $R-Cl + Na-O-CH_2-CH_2-NH_2 \rightarrow R-O-CH_2-CH_2-NH_2 + NaCl$

The dodecenyl-2-aminoethyl ether was evaluated by reaction with various diisocyanates in the presence of JP-4. The results of these tests are listed in Table 41. When Hylene TM-65 was reacted with dodecenyl-2-aminoethyl ether in JP-4, the product was too soluble. It increased the viscosity of the fuel but failed to produce a gel.

In run number 7-28-1, hexamethylene diisocyanate was reacted with the same amine. This system produced a viscoelastic gel that was very similar to the one obtained with 2-ethylhexyl-3-aminopropyl ether and hexamethylene diisocyanate.

When 1,4-bis(isocyanatomethyl) cyclohexane was reacted with dodecenyl-2-aminoethyl ether in JP-4, it slowly (about 6 seconds) converted the fuel to a tough viscoelastic gel. It was noted that this same diisocyanate required 3 to 4 minutes to gel JP-4 when it was reacted with Amine 803. While determining the rate of gelation, it was noticed that with several diisocyanates, the rate of fuel gelation was much faster using dodecenyl-2-aminoethyl ether than was obtained with 2-ethylhexyl-3-aminopropyl ether. It is believed that the rate of gelation is influenced by the location of the ether linkage in the molecule.

Table 42 lists the results obtained using a different type of amine. The amine, delta-aminobutylmethyldiethoxysilane, is soluble in JP-4 and has a low freezing point. In run number 8-2-1, the silane was reacted with menthane diisocyanate in JP-4. This system required about one minute to form a good viscoelastic gel. It is similar to the one obtained with Amine 803 and hexamethylene diisocyanate.

In run number 8-2-2, Hylene TM-65 and the delta-silane rapidly converted the fuel to a weak particulate gel. When the diisocyanate was the 2,6-isomer, the reaction was practically instantaneous. This system produced a gel similar to the one obtained using the same delta-silane and Hylene TM-65.

Analysis of the results obtained with the various gelling agents definitely indicates that the type of fuel gel is influenced by the type of amine and diisocyanate. The aromatic diisocyanates and aliphatic amines tend to give a particulate gel. When these gels are tested under impact conditions, they break into small pieces. When the gels are burned, there is only a small amount of spreading caused by the melting of the surface of the gel. When the aromatic diisocyanates and alkyl-ether-amines are used to gel the fuel, the gel is between a particulate

gel and a viscoelastic gel. This type of gel does not have good strength, therefore no burning or impact tests were made.

When an aliphatic diisocyanate and an alkyl-amino-ether are reacted in JP-4, a tough viscoelastic gel is obtained. On the impact testing apparatus, none of the gelled fuel was thrown from the container. Even though the strength of this gel is excellent, the gel melts on burning, then flows like liquid fuel. Another good system is an aromatic triisocyanate and an aliphatic amine. This system produces a good dilatent gel and does not flow while burning. The disadvantage with this system is that the aromatic triisocyanates are solids having limited solubility in JP-4.

Another observation made with the various systems discussed above is the rate at which the fuel is gelled. In several instances excellent gels were obtained which would undoubtedly contain the fuel under impact conditions, but the time required to obtain the gel was in the order of 3 to 5 minutes. This immediately makes the system of no value to the problem at hand.

Excellent gels were also obtained using the aromatic triisocyanates with both aliphatic amines and alkoxyamines. These gels are dilatent, which is thought to be optimum for the problem at hand. Under stress, several of these gels actually crumbled while others could be "bounced like rubber balls."

A literature search revealed that all aromatic triisocyanates are solids. Since they are solids, they cannot be rapidly injected into fuel. Aliphatic amines and alkoxyamines when reacted with aromatic triisocyanates exhibited excellent impact properties and contained the fuel while burning as well as retarding the burning rate.

The results obtained with the various isocyanates and amines discussed in this section and the aforementioned observations lead to the following conclusions. The system which will rapidly gel jet fuel and produce a gel that will contain the fuel under impact conditions, contain the fuel while burning, and retard the burning rate is a trifunctional amine or isocyanate containing both aromatic rings and ether linkages.

In view of the aforementioned conclusions, efforts were directed toward the preparation of aliphatic triamines containing ether linkages.

The possibility exists that the alkoxy-triamines when phosgenated will yield alkoxy triisocyanates that are liquids. These triamines when reacted with substituted aromatic amines should yield excellent gels.

Various attempts were made to prepare the aliphatic triamines. The initial approach was to cyanoethylate triols such as glycerol and ethylene oxide adducts of triols.

The general reaction is shown as follows:

8. $R(-O-CH_2-CH_2-OH)_3 + 3-CH_2=CH-CN \xrightarrow{\quad OH \quad}$

$R(-O-CH_2-CH_2-O-CH_2-CH_2-CN)_3$

This compound can then be reduced according to the general equation:

9. $R(-O-CH_2-CH_2-O-CH_2-CH_2-CN) \xrightarrow{\quad H \quad}$

$R(-O-CH_2-CH_2-O-CH_2-CH_2-CH_2-NH_2)_3$

Numerous attempts were made to prepare the tri-acrylonitrile addition product of several ethylene oxide adducts of trimethylol propane. Various basic catalysts were also investigated; however, in all cases incomplete cyanoethylation was obtained.

With the cyanoethylated adducts of diols such as 2-ethylhexyl-1, 3-diol, various attempts were made to produce the diamine by reduction, but these failed in that either incomplete reduction was obtained or the product consisted of a mixture of amines.

In view of the difficulty encountered in the aforementioned procedure, it was decided to prepare the ether-amines using the same procedure as was used in preparing dodecenyl-2-aminoethyl ether. Since dodecenyl chloride is a very active halide due to the presence of the olefin group, it was decided to prepare an alkoxyamine using dodecyl bromide and 2-amino sodium ethoxide. The general reaction is as follows:

10. $H_2N-CH_2-CH_2-OH + Na \rightarrow H_2N-CH_2-CH_2-O-Na$

11. $R\text{-}Br + Na\text{-}O\text{-}CH_2\text{-}CH_2\text{-}NH_2 \longrightarrow R\text{-}O\text{-}CH_2\text{-}CH_2\text{-}NH_2$

A competing reaction can also occur. This reaction is as follows:

12. $R\text{-}Br + NaNH\text{-}CH_2\text{-}CH_2\text{-}OH \longrightarrow R\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}OH + Na\,Br$

Analysis showed that 85 weight percent of the product consisted of N-dodecyl-ethanolamine (equation 12) and 15 weight percent was the desired dodecyl-2-aminoethyl ether.

In view of these results, another approach was considered. This involved blocking of the amine prior to preparing the sodium salt. The general reaction is presented below:

13. $(CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-})_2O + HO\text{-}CH_2CH_2NH_2 \longrightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}OH$

Difficulty was encountered with the above amide when attempts were made to prepare the sodium salt using sodium methoxide, as this also cleaved the amide linkage.

In order to avoid this cleavage, the ethanolamine was reacted with phthalic anhydride to produce the following:

14. $HO\text{-}CH_2\text{-}CH_2\text{-}NH_2 + $ $ \longrightarrow $ $ N\text{-}CH_2\text{-}CH_2\text{-}OH$

Efforts to prepare the sodium alkoxide of 2-hydroxyethyl phthalimide were not successful due to the insolubility of the phthalimide derivative in a methanol or an ethanol solution of the corresponding sodium alkoxide.

In view of this difficulty, an attempt was made to prepare the alkoxyamines from 2-bromoethylamine and the sodium salt of a branched diol.

The 2-bromoethylamine is available as the hydrobromide salt. This material was converted to the free amine using ammonia. However,

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when the 2-bromoethylamine is added to the sodium alcoholate, the material splits out H Br and polymerizes to a polyamine.

An attempt was made to block the amine group by converting it to the amide as shown in the following equation:

15. $Br-CH_2-CH_2-NH_2 + (CH_3-\overset{\overset{O}{\|}}{C})_2-O \longrightarrow Br-CH_2-CH_2-NH-\overset{\overset{O}{\|}}{C}-CH_3$

However, in place of obtaining the desired amide, the material splits out H Br and cyclizes to produce the following compound:

$$H_3C-\underset{O}{\overset{N}{C}}$$

In order to avoid this cyclization, phthalic anhydride was used. Cyclization will not occur using this anhydride. The general reaction is shown below:

16. $Br-CH_2-CH_2-NH_2 +$ [phthalic anhydride] $O \longrightarrow Br-CH_2-CH_2-N$ [phthalimide]

When an attempt was made to prepare the 2-bromoethylphthalimide according to equation 16, the 2-bromoethylamine split out H Br and formed a polyamine.

Because of these negative results, it is proposed to use the following approach. The 2-bromoethyl phthalimide can be prepared by reacting potassium phthalimide with 1,2-dibromoethane using dimethyl formamide as the solvent. The reaction is shown as follows:

17.   [phthalimide] $NK + Br-CH_2-CH_2-Br \longrightarrow$ [phthalimide] $N-CH_2-CH_2-Br$

The 2-bromoethyl phthalimide is then reacted with the sodium salt of a diol:

18. [phthalimide structure] N-CH$_2$-CH$_2$-Br + R(-ONa)$_2$ →

$$\left[R - O - CH - CH_2 - N \text{(phthalimide)} \right]_2$$

Hydrolysis of the above product using hydrazine hydrate followed by heating of the hydrazone with dilute HCl will readily yield the corresponding alkoxyamine:

19. $\left[R \ -O-CH_2-CH_2-N \text{(phthalimide)} \right]_2$ $\xrightarrow{\text{1. H}_2\text{N-NH}_2 \cdot \text{HOH} \quad \text{2. HCl}}$

$$R\left[-O - CH_2-CH_2-NH_2 \right]_2$$

Using this procedure, both aliphatic ether amines and aromatic ether amines should be readily synthesized. The amines can be evaluated by reaction with various isocyanates in JP-4 or they can be phosgenated and converted to the corresponding isocyanate. These can then be evaluated by reacting them with other amines.

Of particular interest is the possibility that liquid aromatic triisocyanates can be synthesized by this technique. One example is listed as follows:

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$$+ 3 \text{ Na} \xrightarrow{\text{ROH}}$$

$$3 \text{ Br} - CH_2 - CH_2 - N$$

1. $H_2N - NH_2 \cdot HOH$

2. HCl

It is anticipated that the above triamine is a liquid and can be evaluated as such. It can also be phosgenated to yield a triisocyanate. It is anticipated that this compound is a liquid.

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$$O-CH_2-CH_2-NH_2 \cdot HCl$$

$$HCl \cdot H_2N-H_2C-H_2C-O \qquad O-CH_2-CH_2-NH_2 \cdot HCl$$

$$\xrightarrow{\text{COCl}_2}$$

$$O-CH_2-CH_2-NCO$$

$$OCN-H_2C-H_2C-O \qquad O-CH_2-CH_2-NCO$$

The above triisocyanate has the aromatic ring as well as the ether linkages. This material can be reacted with branched aliphatic amines or alkoxyamines in JP-4. Analysis of the data as discussed in this report indicates that this is the general type of material needed to produce the optimum fuel gel.

FUEL GEL EVALUATION

RATE OF FUEL GELATION

One of the problems concerning the rapid gelation of JP-4 is the development of a technique whereby the rate of gelation with respect to the increase in gel strength can be measured during the first few seconds. A literature search failed to produce a technique fast enough to yield the needed data.

In view of the above findings, experimental work was initiated by the Institute's Department of Electrical Engineering in an effort to determine techniques by which the stiffness of the gel can be measured throughout the time interval from the liquid state to several minutes after the additives are injected into the fuel. Several factors were considered in these tests. In order to obtain the desired data, it was necessary to develop a technique that will not be affected by the stirring prior to the addition of the additives, will not restrict the mixing of the additives, will give a continuous reading with an effective time resolution of much less than one second, will be reproducible, and will be a function only of the stiffness parameter.

With these considerations, the use of ultrasonics appeared to be a good approach if it could be made to yield the stiffness parameter, since little if any obstructions would need to be placed in the mixture. For the first test a continuous wave ultrasonic technique was tried in which two ultrasonic transducers were mounted diametrically opposite each other through holes in the sides of the container in which the JP-4 is to be gelled. A frequency of 500 kc was used to drive one of the transducers, and the other transducer was used as a receiver to produce an output voltage replica of the ultrasonic signal incident on its face. The output voltage level and phase were monitored as the diisocyanate was added to the JP-4 containing the amine. With the additives, the output voltage and phase both changed appreciably and continued to change for several minutes. This looked like a usable method except that the received amplitude and phase were very critical functions of frequency, and there was no direct way of relating the observed change with gel stiffness.

To reduce some of the above problems and to allow separation of some of the variables, another test arrangement was made which also

used ultrasonics; but, instead of applying a continuous wave to the transmitting transducer, a pulse was used. The use of widely spaced pulses allowed transit times between the transducers to be measured and eliminated the standing wave problem. Since the propagation velocity contains a stiffness term, it was thought that the transit time parameter could possibly be measured to show changes in stiffness. The test vessel (a round aluminum container) was modified to have flats diametrically opposed to each other against which the transducers were placed. This permitted operation with no appreciable projections in the mixing chamber. The transit time was 55 microseconds through the liquid JP-4; when gelled, the transit time increased only to 56 microseconds and remained at this value. This change is considered to be too small for effective use of this technique as a measurement of gel rigidity. The amplitude of the ultrasonic pulse through the material decreased only about 10 percent immediately upon change from a liquid to a gel state. The amplitude continued to decrease slowly, and after an hour it was down to about one-tenth of the value observed through the liquid. This continued change is undoubtedly due to the continued reaction of the additives.

Since the tests conducted with ultrasonics failed to disclose a suitable measurement technique, a procedure was developed that will yield the approximate rate of gelation. Although these data are not exact, they do represent an approximate rate of gelation and permit one to compare the various systems. The procedure consisted of dissolving one reactant in jet fuel and the second reactant in another portion of jet fuel. The two solutions were then introduced into a glass tube. By previously determining the flow rate through the tube, it is possible to determine the rate of gelation by determining how far down the tube the mixture passes before gelation occurs.

During a steering committe meeting, it was decided that various tests be designed in order to compare the various gelling systems. The tests should include such properties as the rate of gelation, impact properties, burning properties, gel rigidity, and sparkignition properties.

It should be noted that during the course of this program numerous systems were developed for the gelation of jet fuel. Some of the systems produced tough gels that displayed excellent impact and burning properties. Such a system is an aromatic triisocyanate or a substituted aromatic diisocyanate with an aliphatic amine or an

alkoxyamine. However, the rates of gelation were in the range of 3 to 5 minutes at room temperature and as such would not apply to the rapid gelation of fuel. In an effort to rate those systems that had a reasonable rating in all of the tests, only those systems were evaluated that gelled jet fuel in less than 10 seconds.

Table 43 lists the rates of gelation for various gelling systems using a total additive concentration of 4 weight percent. It can be noted that the most rapid gelation rate was obtained with β-ethoxy-ethylamine and 4, 6-dimethyl-1, 3-xylylene diisocyanate (run number 8-43-3). This additive system gelled the fuel in 0.04 second. If one observes the rates of gelation using 4-chlorobenzylamine with m-xylylene diisocyanate or 4, 6-dimethyl-1, 3-xylylene diisocyanate (runs numbered 8-43-1 and 8-43-6, respectively), it can be noted that the presence of the methyl groups on the diisocyanate caused a three-fold increase in the rate of fuel gelation.

The same additive systems were re-evaluated at a total additive concentration of 2.5 weight percent. The results of these tests are listed in Table 44. If one compares the rates of gelation using a total additive concentration of 2.5 weight percent with those obtained of the 4.0 weight percent level, it can be noted that the rates of gelation for a particular system are essentially the same.

BURNING PROPERTIES

One very important property of gelled JF-4 is how the gel performs once it is ignited. During the course of this program a cursory study was made of the burning properties of the various gels regardless of their gelation rate.

This study consisted of placing the gelled JP-4 on a transite board or on the ground and igniting it. The transite board was used in order to better observe the flow properties of the burning gel. The burning characteristics of the gel were noted as well as the burning time. The results of these tests are listed in Table 45.

When 100 grams of the hexamethylene diisocyanate-oleyl amine gelled JP-4 was burned (run number 6-39-1), the burning time was 8 minutes. The gel when placed on the transite was in the shape of a cylinder 2 inches in diameter. While burning, the surface of the gel melted and flowed over an area approximately 12 inches in diameter.

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In run number 6-39-2, the fuel was gelled using toluene diisocyanate and lauryl amine. The burning time for this gel was 9 minutes. Initially, the gel covered an area 2 inches in diameter. While burning, the gel flowed over an area approximately 4 inches in diameter. The gelled fuel did not melt while burning but merely bubbled and released vapors of JP-4.

When the hexamethylene diisocyanate-Amine 803 gelled fuel was placed on the transite board, this tough viscoelastic gel slowly flowed over an area approximately 4 inches in diameter. The burning time was 3 minutes. Once ignited, the entire mass of gel melted and flowed over an area of approximately 15 to 18 inches.

In run number 6-39-4, the burning characteristics were determined for a 2, 4, 6-toluene triisocyanate-Amine 803 gelled fuel. This dilatent gel when placed on the transite board slowly flowed over an area 6 inches in diameter and was about 0.5 inch thick. When ignited, the gel merely bubbled and released vapors of JP-4. It did not melt while burning.

When the 4-methoxy-m-phenylene diisocyanate-Amine 803 gelled fuel was ignited, it burned for a total of 5 minutes. Once ignited, the fuel exuded from the gel and flowed over an area 15 to 18 inches in diameter. This test is listed as run number 6-41-1 in Table 45.

In run number 7-38-1, Hylene TM-65 and 2-ethylhexylamine were used to gel JP-4. This system formed a weak viscoelastic gel which had no form integrity. While burning, the gel flowed over an area approximately twice the size it occupied originally. The burning time was 7 minutes for 100 grams of gel.

Another viscoelastic gel was obtained with the hexamethylene diisocyanate-dodecenyl-2-aminoethyl ether system (run number 7-38-3). However, when this gel was ignited, it melted and flowed like a liquid.

The gel obtained with menthane diisocyanate and lauryl amine was not considered one of the better gels since it had a consistency similar to a heavy grease. However, it did have excellent burning properties. This gel, while burning, did not melt or flow. It contained the fuel and appeared to boil as the fuel vaporized and escaped through the gel. The burning time was 6 minutes for 100 grams of gel.

In runs numbered 7-43-1A, 7-50-2A, and 8-1-1A, the 3-chloro-phenyl isocyanate-4-chlorobenzyl amine system was evaluated at total additive concentrations of 4 percent, 2 percent, and 1 percent. By observing the results as listed in Table 45, it can be noted that the gel containing 1.0 weight percent total additives burned as well as those containing the 2-percent and 4-percent additives.

In run number 8-6-1A, the gelling system was m-xylylene diisocyanate and p-phenetidine. Although this system has an extremely slow gelation rate, it has excellent burning properties in that it did not flow while burning. The burning time was 13 minutes.

During the latter phase of the program, burning tests were made on those systems that had a gelation rate of 10.0 seconds or less. These data were obtained in order to compare the various gelling agents. With respect to those systems previously discussed, some were repeated provided they gelled JP-4 in less than 10 seconds. It can also be noted that some of the gelling systems eliminated had excellent burning properties as shown in the previous discussion, but the rates of gelation were too slow.

In order to standardize the procedure for this study, 100 grams of gelled fuel was used in all the tests. The gel was cylindrical in shape, 2.0 inches in diameter and 2.5 inches in height. Two properties of the burning gel were recorded. One was the time required to burn the gel completely, and the second was the increase in area due to melting of the gel. Table 46 lists the results of the burning tests for various gelling systems using a total additive concentration of 4.0 weight percent. In run number 8-45-2, the additives were 4-isopropyl-benzylamine and 4,6-dimethyl-1,3-xylylene diisocyanate. This system converts the JP-4 into a dry particulate gel. The gel has good burning properties in that a time of 16.0 minutes was required to burn 100 grams of gel. While burning, the gel did not melt but remained a dry solid. Several other additive systems listed in Table 46 had good burning properties in that they did not flow while burning and required 15.0 minutes or more to consume the fuel.

Run number 8-45-7 lists an example of the burning properties of a viscoelastic gel. In this run, 2-ethylhexyl-3-aminopropyl ether and hexamethylene diisocyanate were used as the gelling agents. Although this gel has excellent impact properties, its burning properties are poor. This gel burned in only 4 minutes and flowed over an area 10 times that occupied by the gel prior to ignition.

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Table 47 lists the burning properties of the same gelling systems; however, the total additive concentration was decreased to 2.5 weight percent. If one compares the results obtained at the 2.5 weight percent level with the 4.0 weight percent level, it can be noted that those systems which did not melt using 4.0 weight percent additives likewise did not melt at 2.5 weight percent additives. With those systems that did melt using 4.0 weight percent, it can be noted that when the concentration was decreased to 2.5 weight percent, the gels melted and covered a slightly larger area. In addition, these gels burned at a faster rate.

IMPACT PROPERTIES

The main objective of fuel gelation is to develop a system that will contain the fuel should a fuel tank be ruptured in a crash. In view of this, one important test is to determine how the various fuel gels perform under impact conditions. Figure 1 is a schematic of the test equipment used to obtain the impact data. The front of the container used in this test equipment has an opening 1.5 inches long and 0.5 inch wide. The opening is taped shut and the fuel is gelled in the container. The tape is removed and the arm on which the container is mounted is pulled parallel to the base. This places tension on the spring. When released, the arm and container are pulled upward by the spring and strike the crossbar, which abruptly stops the forward motion.

The speed at which the container travels was determined by a high speed camera. Two movies were taken, one when the arm was drawn back 45° from the crossbar, and another when the arm was drawn back 90°. It was determined that when the arm was drawn back 45° from the crossbar and released, the speed immediately before impact was determined to be 6.45 mph. When the arm was drawn back 90° before release, the speed immediately before impact was 9.5 mph.

Since several assumptions were necessary in order to determine the approximate force of impact, the calculations used to determine this force when the arm was released at the 45° angle are as follows.

At 45° the speed immediately before impact was determined to be 6.45 mph; therefore,

$$\frac{6.45 \text{ mi}}{\text{hr}} \times \frac{5280 \text{ ft}}{\text{mi}} \times \frac{\text{hr}}{3600 \text{ sec}} = 9.46 \text{ ft/sec}$$

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The arm strikes a 1/8-inch rubber gasket mounted on the cross-bar. Assume that the 1/8-inch rubber gasket is compressed to 1/16 inch during impact. This means that the forward motion is stopped over a distance of 1/16 inch. Therefore,

$$1/16 \text{ in.} = 0.0625 \text{ in.} = 0.0625 \text{ in.} \times \frac{ft}{12 \text{ in.}} = 0.0052 \text{ ft}$$

Since the initial speed (v_i) was 9.46 feet/second and the final velocity (v_f) was 0, and assuming that the rate of deceleration was constant, then the average velocity (v_a) during deceleration is

$$v_a = \frac{v_i - v_f}{2} = \frac{9.46 - 0}{2} = 4.73 \text{ ft/sec}$$

and the time to travel 0.0052 feet is

$$\frac{\text{sec}}{4.73 \text{ ft}} \times 0.0052 \text{ ft} = 0.0011 \text{ sec}$$

The deceleration (a) on impact is then determined by the following:

$$a = \frac{v}{t} = \frac{9.46 \text{ ft}}{\text{sec}} \times \frac{1}{.0011 \text{ sec}} = 8600 \text{ ft/sec}^2$$

Expressing this in terms of gravity,

$$8600 \text{ ft/sec}^2 \times \frac{1}{32} = 268 \text{ G's}$$

Using similar calculations and making the same assumptions, the impact force applied to the gel when the arm was released 90° from the crossbar was calculated to be approximately 580 G's.

During the course of the program as new gels were developed, they were evaluated on the impact equipment. The results of these evaluations are compiled in Table 48. In run number 6-21-1, the lauryl amine-Hylene TM-65 gelled fuel under an impact force of 268 G's lost 11.0 grams of fuel. The gel was thrown forward out of the opening in the container. It broke into small pieces, which splattered on hitting the ground.

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In run number 6-22-2, the oleyl amine-hexamethylene diisocyanate gelled fuel lost 9.0 grams under the same impact force. When the test was repeated as shown in run number 6-45-1, 8.0 grams of fuel were lost.

Amine 803 and hexamethylene diisocyanate, when used at a total concentration of 4.0 weight percent, converts JP-4 into a viscoelastic gel. In run number 6-45-2, this gel was tested under impact conditions. When the gel was subjected to an impact force of 580 G's, the gel remained in the container. When this same gel was tested a second time, a small quantity of the gel was extruded through the opening and hung over the edge of the hole. During both impacts none of the gel was thrown free of the hole.

In an effort to make the test more severe, the opening in the container was increased from 1.5" X 0.5" to 2.5" X 5/8". The impact force on all the tests was 580 G's.

In addition, the equipment was designed so that the gel when thrown from the container flew through a flame depth of approximately 10 inches. Screening tests showed that using a flame depth of much less than 10 inches resulted in no ignition on any of the systems. The impact force used to evaluate the gels was 580 G's. The results of these tests are listed in Table 49. In run number 8-14-1, 4-chloro-benzylamine and m-xylylene diisocyanate were used to convert JP-4 to a dry particulate gel. The gel had little cohesive strength. On impact, the gel lost 23 grams. The gel particles when thrown through the flame ignited and continued to burn on hitting the ground.

In run number 8-14-2, delta-aminobutylmethyldiethoxysilane and menthane diisocyanate converted JP-4 into a gel that was elastomeric in nature. Even though this gel will melt and flow like liquid fuel when once ignited, 14 grams of the gel was thrown from the container and through the flame without igniting.

In run number 8-22-1, Amine 803 and hexamethylene diisocyanate converted JP-4 to a tough viscoelastic gel. Under an impact force of 580 G's, this system contained all of the fuel. It should be pointed out that, even though this gel did contain the fuel, once ignited, the gel melts and flows like liquid fuel.

On examination of the results obtained from the impact tests as listed in Table 49, it can be noted that some gels lost as high as 9 percent of the gelled fuel, some ignited, and some of the gels did not lose any of the fuel.

It was previously stated that a series of evaluation tests were made in an effort to compare the various gelling systems. This series of tests included the impact test. The gels evaluated in these tests had a gelling rate of less than 10 seconds. The impact properties of these gels are listed in Tables 50 and 51.

As previously stated, the front of the container containing the fuel had an opening 2-5/8 inches in length and 5/8 inch in width. The impact force used to evaluate these gels was 580 G's. Table 50 lists the results obtained using a total additive concentration of 4.0 weight percent, and Table 51 lists the results obtained using 2.5 weight percent additives. It can be noted that the viscoelastic-type gels contained all of the fuel under impact conditions at both 4.0 weight percent and 2.5 weight percent additives. These tests are listed as run numbers 9-7-3 and 9-7-4 in Table 50 and 9-4-6 and 9-4-7 in Table 51, respectively.

TEMPERATURE LIMITS FOR VARIOUS GELLING SYSTEMS

The various gelling systems are usually screened at ambient temperatures. Since the gelling system must apply over a wide temperature range, the more promising gelling systems were evaluated at various temperatures in order to determine the maximum and minimum temperatures over which the system can be used effectively. The procedure used was to cool or heat JP-4 to the desired temperature. The two additives were then rapidly added with stirring. The temperature limits recorded are those that were considered the maximum and minimum temperatures over which the gelling system will operate effectively.

In runs numbered 6-2-1A and 6-2-5 as listed in Table 52, it is noted that the temperature range for the hexamethylene diisocyanate-oleyl amine system is from -10°C to 40°C.

Lauryl amine when reacted with hexamethylene diisocyanate also gelled JP-4; however, the gel was not as firm as was obtained when oleyl amine was reacted with hexamethylene diisocyanate. In an effort to determine the effect of temperature on this system, in run number 6-3-3A the temperature of the fuel was lowered to 0°C. At this

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temperature no gel was obtained because the lauryl amine is not soluble in JP-4. This experiment also indicates that the Hylene TM-65-lauryl amine system probably will not work at temperatures 0°C or below because of the insolubility of the amine at these temperatures.

With the hexamethylene diisocyanate-2-ethylhexyl-3-aminopropyl ether system, the temperature range was from -58°C to 60°C.

In run number 8-34-1, delta-aminobutylmethyldiethoxysilane and 4, 6-dimethyl-1, 3-xylylene diisocyanate were added to jet fuel heated to 65°C. The additives immediately converted the fuel to a good gel. When the fuel was cooled to -40°C prior to adding the reactants (run number 8-34-2), the additives rapidly gelled the fuel. It is thought that this is the lower limit, because the gel lost some of its cohesive strength.

When 4-6-dimethyl-1, 3-xylylene diisocyanate was reacted with oleyl amine in JP-4 heated to 65°C, it rapidly converted the fuel to a gel. At the lower temperature range, it was determined that the minimum temperature at which this system will operate is -27°C (run number 8-34-3A).

When ethoxyethylamine and 4, 6-dimethyl-1, 3-xylylene diisocyanate were reacted in JP-4 heated to 65°C, the rate of gelation was entirely too fast to obtain good mixing. By placing each additive into half of the fuel and then rapidly pouring the two solutions into a third container, a good gel was obtained at the aforementioned temperature.

When the same reactants were mixed as described above at -40°C, the additives instantaneously formed a particulate gel.

During this phase of the program, a series of temperature limits screening tests were made on a series of fuel gels in order that the various systems can be compared. In this comparison, only those systems were evaluated that would gel JP-4 in less than 10 seconds. The results of these tests are listed in Table 53. These gels were evaluated using a total additives conncentration of 4. 0 weight percent. No attempt was made to determine the temperature limits for gels containing 2. 5 weight percent additives.

GEL RIGIDITY

During the course of this investigation various types of fuel gels were developed. These included gels that were particulate, thixotropic, dilatent, and viscoelastic. In an effort to obtain some comparative data, a test was designed that would measure the rigidity of the gel. This test involves the use of a Hunter Mechanical Force Gage Model No. L-500-M. On the tip of the gage is mounted a disc having a surface area of one square inch. The procedure used is to place the gage disc on the surface of the gel. Pressure is slowly applied and the instrument measures the applied pressure in grams. The applied pressure gradually increases until the gel breaks at which time the gage records a sudden drop in applied pressure. The maximum applied pressure is recorded as the gel hardness. This comparative test cannot be used on viscoelastic gels. With viscoelastic gels, as pressure is applied to the disc, the gel yields and no maximum pressure can be observed.

The results of these are listed in Table 54. In run number 7-2-1, the hexamethylene diisocyanate-Amine 803 system produces a viscoelastic gel at room temperature; however, when the fuel is gelled at -58°C, the gel is no longer viscoelastic and has a hardness of 900 grams/inch^2 at this temperature.

In run number 7-43-1B, JP-4 was gelled using 3-chlorophenyl isocyanate and 4-chlorobenzyl amine. This system forms a firm particulate gel. It has a hardness rating of 125 grams/inch^2.

In run number 8-6-1B, the gelling system was m-xylylene diisocyanate and 4-chlorobenzyl amine. The total additive concentration was 4.0 weight percent. This system instantaneously forms a firm, dry particulate gel. It had a hardness of 395 grams/inch^2. When the additive concentration was decreased to 2.0 weight percent, there was little change in the hardness of the gel (run number 7-50-2B).

In run number 8-28-1A, 4-chlorobenzylamine and 4-6-dimethyl-1,3-xylylene diisocyanate form a dry particulate gel in JP-4. The gel has little cohesive strength and is readily broken under shear. However, with respect to the penetrometer tests, it had a hardness of 600 grams/inch^2. Lauryl amine and the same diisocyanate likewise instantaneously formed a good particulate gel with a firmness of 600 grams/inch^2.

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SPARK IGNITION PROPERTIES OF GELLED FUELS

During a plane crash, one great source of fire is caused by flying debris. The debris on hitting the landing strip will spark and ignite vaporized fuel if it is present. In view of this, a test was made on the various gelled fuels in order to determine the effect of gelation on the rate of hydrocarbon vaporization and spark ignition.

A schematic of the equipment used to determine the spark ignition properties of the various gels is shown in Figure 2. The gel when placed in the container has a surface area of 31.0 cm^2. The cross-sectional area of the container is 10.0 cm^2, and the area of the exit orifice is 0.7 cm^2. The air velocity is measured with a flow meter. The procedure consists of starting the air flow across the gel, and 2 seconds later a spark is continually thrown across the exit orifice using a Tesla coil. The data recorded is the maximum air flow in which the vapors can be ignited with the Tesla coil.

Table 55 lists the results obtained using a total additive concentration of 4.0 weight percent. For comparison purposes, in run number 9-11-1, a spark ignition test was run on JP-4. It can be noted that JP-4 required 20 liters of air per minute before the velocity was great enough to decrease the concentration of vaporized hydrocarbon below the explosive limits.

If one analyzes the results as listed in Table 55, it can be noted that gelling the fuel significantly decreases the rate of hydrocarbon vaporization. The three best gels were the lauryl amine-Hylene TM-65 system, 4-chlorobenzylamine-4,6-dimethyl-1,3-xylylene diisocyanate system, and the "Delta" silane-menthane diisocyanate system. These runs are listed as 9-13-5, 9-11-3, and 9-13-4 respectively.

The spark ignition tests were also run on the same gelling systems using a total additive concentration of 2.5 weight percent. The results of these tests are listed in Table 56. Analysis of the results show that, at the lower additive concentration, the gels are slightly more flammable than at the 4.0 weight percent level; however, the rate of vaporization is still significantly less than was obtained with JP-4.

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COMPARATIVE EVALUATION OF VARIOUS GELS

It was previously stated that during the latter phase of the program, various tests were designed in order to evaluate the various gels with respect to rate of gelation, gel strength (where applicable), burning properties, temperature limits, spark ignition properties, and performance of the various gels under impact conditions.

The code used to compare the various gels is listed in Table 57. With respect to gel rigidity, only the particulate or dilatent gels could be evaluated since the viscoelastic gels will flow when pressure is applied to the surface of the gel. Since these gels were not rigid enough to obtain a penetrometer reading, they were assigned a rating of 1.

Only those gelling systems were evaluated that had a gelation rate of 10 seconds or less. Several gelling systems developed during this program had excellent strength and burning properties; however, they were not included in this gel comparison study since their rates of gelation were too slow.

With respect to the temperature range over which the various gelling systems will apply, the rating assigned to the gels not only included the temperature range but also the effect of temperature on the rate of gelation as well as any adverse effects on the properties of the gels.

When the burning characteristics of the gels were evaluated, two properties were considered. One is the time required to burn the gelled JP-4. The second property is if the gel melted while burning, the area over which it flowed was recorded.

Table 58 lists the comparative ratings for the various gels using a total additives concentration of 4.0 weight percent. If one examines the data as listed in Table 58, it can be noted that several systems received excellent ratings in certain tests; however, no system received an excellent rating in all of the tests.

Of the various systems evaluated, Table 58 indicates that the 4-chlorobenzylamine-4, 6-dimethyl-1, 3-xylylene diisocyanate is the best system since it was rated at 64 out of a possible 70. It should be

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pointed out that even though the viscoelastic gels were excellent under impact conditions and despite their rate of gelation, they received a lower rating because the gel rigidity could not be determined.

Table 59 lists some comparative tests made on the same gelling systems at a total additive concentration of 2.5 weight percent. Not all of the tests were made on the gels containing 2.5 weight percent additives. The tests include the rate of gelation, impact properties, burning properties, and the spark ignition tests. By observing the results as listed in Table 59, it can be noted that the gels containing the 2.5 weight percent additive were not rated as high as were the ones containing 4.0 weight percent additives.

After carefully evaluating the results obtained from the comparative tests, it was noted that several of the additive systems performed exceptionally well in two or more of the tests. These systems gelled the fuel in less than one second and are considered to be the most promising systems developed during this program.

Additive System	Impact Performance	Temp. Range	Burning Properties	Spark Ignition
Dodecenyl-2-aminoethyl ether Hexamethylene diisocyanate	X	X		X
2-Ethylhexyl-3-aminopropyl ether Hexamethylene diisocyanate	X	X		X
4-Chlorobenzylamine m-Xylylene diisocyanate		X	X	X
Hexylamine 4,4-Dimethyl-1,3-xylylene diisocyanate		X	X	X
4-Chlorobenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate		X	X	X

The first two systems listed above form viscoelastic gels in JP-4. These gels excel in their impact performance, temperature range and inhibition of spark ignition; however, they had poor burning properties. The latter three gelling systems form particulate gels. These gels excel in temperature range, burning properties, and inhibition of spark ignition.

The development of an additive system which would combine the impact properties of the viscoelastic gels and the burning properties of the particulate gels would yield the optimum system for the rapid gelation of aircraft fuels.

TOXICITY OF ADDITIVES

The liquid isocyanates are, in general, irritating to the mucous membranes and the skin. When handling these materials, one should use adequate protection for the skin and eyes. All work with these materials should be carried out in a well-ventilated area. All contaminated skin areas should be washed with soap and water.

The organic amines are bases and may cause irritation if allowed to remain on the skin in an undiluted form. Usually, no effects are experienced, although some persons are more susceptible than others. In case of direct contact, it is recommended that the excess be wiped off with a cloth which can be discarded. The contact area should be washed with dilute acetic acid or vinegar and rinsed with water, followed by washing with soap and water.

EXPERIMENTATION

The following is a list of the various types of compounds synthesized during the course of this program. This list does not contain all of the compounds synthesized; however, it does contain a typical example for each class or type of compound synthesized.

PREPARATION OF TETRAMETHYLENE DIISOCYANATE

In a round-bottom flask equipped with a gas dispersion tube, nitrogen sweep gas system, stirrer, thermometer, and condenser, were placed 100 grams (1.13 mole) of tetramethylene diamine and 1500 ml of o-dichlorobenzene. Anhydrous hydrogen chloride was then bubbled into the rapidly stirred solution until the diamine was converted to the dihydrochloride. The system was then swept with nitrogen to remove the excess hydrogen chloride.

Phosgene was then bubbled into the rapidly stirred solution for 1.0 hour at room temperature. The temperature was then raised to reflux, and the phosgenation was continued for 13.0 hours. The system was then swept for 1.0 hour with nitrogen and cooled to room temperature. The mixture was then filtered, and the pure diisocyanate was obtained by fractional distillation. The boiling point was 101°C at 11.0 millimeters of mercury. The yield was 61 percent. NCO analysis: theoretical, 60.0 percent; found, 59.4 percent.

PREPARATION OF 1, 3, 5-BENZENE TRIISOCYANATE

98.8 grams (0.425 mole) of benzene triamine trihydrochloride and 0.6 liter of xylene were placed in a round-bottom flask equipped with a gas dispersion tube, nitrogen sweep gas system, stirrer, thermometer, and condenser. The system was swept with dry nitrogen for 0.25 hour at room temperature. Phosgene was then bubbled into the rapidly stirred mixture for 0.5 hour. The temperature was raised to reflux, and phosgenation was continued for 7 hours. The mixture was then swept with nitrogen for 1 hour, cooled to room temperature, and filtered. The solvent was removed by distillation, and the crude triisocyanate was purified by crystallization from a toluene-hexane mixture. The melting point was 70 to 75°C.

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PREPARATION OF 2, 4, 6-TOLUENE TRIISOCYANATE

In a round-bottom flask equipped with a gas dispersion tube, nitrogen sweep gas system, stirrer, condenser, and water trap, were placed 98.0 grams (0.397 mole) of 2, 4, 6-toluene triamine trihydrochloride and 1.0 liter of o-dichlorobenzene. The diamine dihydrochloride was dried by azeotroping the water.

Phosgene was then bubbled into the rapidly stirred mixture for 0.5 hour at room temperature. The temperature was then raised to reflux, and phosgenation was continued for 7 hours. The system was swept with nitrogen for 1 hour, cooled to room temperature, and filtered. The solvent was removed by distillation, and the crude triisocyanate was purified by recrystallization from a benzene-hexane mixture. The yield was 61 percent. Melting point: reported, 75°C; found, 70-72°C.

PREPARATION OF 4-METHOXY-m-PHENYLENE DIISOCYANATE

A mixture consisting of 100 grams (0.474 mole) of 4-methoxy-m-phenylene diamine dihydrochloride and 900 milliliters of o-dichlorobenzene was added to a round-bottom flask equipped with a gas dispersion tube, nitrogen sweep gas system, thermometer, stirrer, and condenser. Phosgene was bubbled into the rapidly stirred solution for 1.0 hour at room temperature. The temperature was then raised to reflux, and phosgenation continued for 4 hours. The system was then swept with nitrogen for 1 hour and cooled to room temperature. The mixture was filtered and the solvent removed by distillation. The crude diisocyanate was purified by recrystallization from hexane at 0°C. Yield: 59 percent

PREPARATION OF 1-CHLORO-2, 4-BENZENE DIISOCYANATE

In a round-bottom flask equipped with a thermometer, gas dispersion tube, stirrer, condenser, and a nitrogen sweep gas system, were placed 89.0 grams (0.62 mole) of 1-chloro-2, 4-benzene-diamine, and 1000 milliliters of xylene. Anhydrous hydrogen chloride was then bubbled into the stirred solution until the diamine was converted to the dihydrochloride. The system was then purged with nitrogen until the excess hydrogen chloride was removed.

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Phosgene was then bubbled into the rapidly stirred suspension, and the temperature was raised to reflux. The phosgenation reaction was continued for 7 hours. The system was then purged with nitrogen, cooled to room temperature, and filtered. The pure diisocyanate was obtained by fractional distillation. The boiling point was 105°C at 1.4 millimeters of mercury. NCO equivalent: theoretical, 43.2 percent; found, 43.0 percent.

PREPARATION OF m-PHENYLENE DIISOCYANATE

In a round-bottom flask equipped with a thermometer, stirrer, gas dispersion tube, condenser, and nitrogen sweep gas system, were placed 100 grams (0.55 mole) of m-phenylene-diamine dihydrochloride and 0.9 liter of xylene.

Phosgene was bubbled into the rapidly stirred mixture for 0.5 hour at room temperature. The temperature was then raised to reflux, and phosgenation continued an additional 7.5 hours. The system was purged with dry nitrogen for 1.0 hour, cooled to room temperature, and filtered. The pure diisocyanate was obtained by fractional distillation. Yield: 81.5 percent. The boiling point was 102-3°C at 9.2 millimeters of mercury. The melting point was 48-50°C.

PREPARATION OF 1, 4-BIS(ISOCYANATOMETHYL) CYCLOHEXANE

A mixture consisting of 71.0 grams (0.5 mole) of 1, 4-bis(amino-methyl) cyclohexane, 0.9 liter of o-dichlorobenzene, and 0.1 liter of benzene was placed in a round-bottom flask equipped with a gas dispersion tube, nitrogen sweep gas system, thermometer, stirrer, condenser, and water trap. The mixture was dried by distilling off the benzene-water azeotrope.

The water trap was removed, and anhydrous hydrogen chloride was bubbled into the rapidly stirred solution until the diamine was converted to the corresponding dihydrochloride. The system was then purged with nitrogen to remove the excess hydrogen chloride.

Phosgene was then bubbled into the rapidly stirred solution for 0.5 hour at room temperature. The temperature was raised to reflux, and phosgenation continued for 6.0 hours. The system was purged with nitrogen for 1.0 hour, cooled to room temperature, and filtered. The pure diisocyanate was obtained by fractional distillation. The boiling point was 119°C at 1.9 millimeters of mercury. Yield: 77 percent.

PREPARATION OF MENTHANE DIISOCYANATE

In a round-bottom flask equipped with a gas dispersion tube, thermometer, nitrogen ...ep gas system, stirrer, condenser, and water trap, were placed 85.2 grams (0.5 mole) of menthane diamine, 1.5 liter of o-dichlorobenzene, and 0.1 liter of benzene. The mixture was dried by distilling off the benzene-water azeotrope.

The diamine dihydrochloride was obtained by bubbling anhydrous hydrogen chloride into the rapidly stirred solution. After the reaction was complete, the excess hydrogen chloride was removed by purging with nitrogen.

Phosgene was then bubbled into the rapidly stirred slurry of the diamine dihydrochloride for 1.0 hour at room temperature. The temperature was then raised to reflux and phosgenation continued for an additional 6.0 hours. The system was then purged with nitrogen for 1.0 hour, cooled to room temperature, and filtered. The pure diisocyanate was obtained by fractional distillation. The boiling point was 86 to 88°C at 0.7 millimeter of mercury. Yield: 74.4 percent.

PREPARATION OF 2-ETHYLHEXYL-2-CYANOETHYL ETHER

A mixture consisting of 520 grams (4.0 mole) of 2-ethylhexanol and 26.0 grams of potassium hydroxide in 29.0 grams of water was placed in a round-bottom flask equipped with a stirrer, thermometer, and dropping funnel. The flask was placed in an ice-bath and the mixture cooled to 20°C. 212 grams (4 moles) of acrylonitrile was then added by drops, maintaining a temperature range of 28 to 32°C. After the addition of the acrylonitrile was completed, the solution was heated at 40°C for 4 hours.

The nitrile was extracted with 0.3 liter of methylene dichloride. The organic phase was separated and washed with dilute hydrochloric acid and then with aqueous sodium bicarbonate. The organic layer was separated and dried over magnesium sulfate. The pure 2-ethylhexyl-2-cyanoethyl ether was obtained by fractional distillation. The boiling point was 101°C at 2.0 millimeters of mercury. Yield: 49 percent.

PREPARATION OF 2-ETHYLHEXYL-3-AMINOPROPYL ETHER. NO. 1

A mixture consisting of 30.0 grams (0.264 mole) of 2-ethylhexyl-2-cyanoethyl ether, 10 grams (0.264 mole) of sodium borohydride, 20 milliliters of tetrahydrofuran, and 50 milliliters of diglyme was placed in a roundbottom flask equipped with a stirrer. thermometer, dropping funnel, and condenser. A solution containing 17.4 grams (0.13 mole) of aluminum chloride was added by drops, maintaining a temperature of 23 to 27°C. After the solution was stirred for 1.0 hour, an additional 10.0 grams (0.075 mole) of aluminum chloride dissolved in 70 milliliters of tetrahydrofuran and 70 milliliters of diglyme was added, and the stirring was continued for another hour.

The solvents were removed by distillation. The residue was poured into ice water and then acidified with dilute sulfuric acid. The organic layer was then washed with dilute sodium hydroxide, separated, and dried over magnesium sulfate. The pure 2-ethylhexyl-3-aminopropyl ether was obtained by fractional distillation. The boiling point was 78 to 80°C at 0.7 millimeter of mercury. Yield: 64 percent.

PREPARATION OF 2-ETHYLHEXYL-3-AMINOPROPYL ETHER. NO. 2

In a round-bottom flask equipped with a thermometer, stirrer, and dropping funnel, were placed 0.6 liter of dry dioxane and (2.0 mole) of sodium. The mixture was heated to reflux and rapidly stirred to produce a fine molten dispersion of sodium. 202.7 grams (2.7 mole) of 3-aminopropanol was added by drops over a 2.0-hour period. The mixture was held at reflux temperature an additional 16.0 hours with stirring. After cooling the mixture, 401.0 grams (2.7 mole) of 2-ethylhexyl chloride was added by drops over a 3.0-hour period. The mixture was then heated under reflux for 13 hours. The cooled mixture was diluted with benzene, water washed. and dried over sodium sulfate. The pure 2-ethylhexyl-3-aminopropyl ether was obtained by fractional distillation. The boiling point was 60 to 65°C at 0.5 millimeter of mercury. Yield: 33 percent

PREPARATION OF DODECENYL-2-AMINOETHYL ETHER

In a round-bottom flask equipped with a thermometer, stirrer, and dropping funnel, were placed 34.5 grams (1.5 mole) of sodium and 0.5 liter of dry dioxane. The mixture was heated to reflux with rapid stirring. Then 100.0 grams (1.8 mole) of ethanolamine was

added by drops. After the addition was completed, the mixture was stirred under reflux for 14.0 hours.

The mixture was then cooled to 11 to 15°C, and 303.8 grams (1.5 mole) of 1-chloro-5, 5, 7, 7, -tetramethyl-2-octene was added by drops over a 2.0-hour period. The mixture was then stirred for 5.0 hours, maintaining a temperature of 25°C. At the end of this period, the temperature was raised to reflux and stirring continued an additional 3.0 hours. The cooled mixture was diluted with benzene, water washed, and dried over magnesium sulfate. The pure dodecenyl-2-aminoethyl ether was obtained by fractional distillation. The boiling point was 78 to 84°C at 0.3 millimeter of mercury. Yield: 71 percent.

LITERATURE SEARCH

Included in the scope of this contract was a literature search concerned with the gelation of hydrocarbons. This literature search revealed that the major effort concerning the gelation of hydrocarbons was related to the preparation of napalm or gels that would apply to flame throwers. The greatest proportion of the literature references were related to the aforementioned applications and did not apply to the rapid gelation of aircraft fuels. As a result, the literature search is included as Appendix III.

DISTRIBUTION

US Army Materiel Command	5
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Bureau of Safety, Civil Aeronautics Board	2
Aviation Research and Development Services, FAA	2
US Army Board for Aviation Accident Research	5

TABLE 1

ATTEMPTED GELATION OF JP-4 USING ADIPYL CHLORIDE AND VARIOUS AMINES

Run No.	Wt % Acid Chloride	Amine	Wt % Amine	Wt % Total Additives	Remarks
5-38-1	2.0	Diam 21* (N-Coco-1,3-propylene diamine)	2.0	4.0	Slight increase in viscosity.
5-38-2	2.0	Lauryl amine	2.0	4.0	Formed a thin slurry.
5-38-3	2.0	Diam 11* (N-Oleyl-1,3-propylene diamine)	2.0	4.0	No apparent change.
5-38-4	2.0	Ethomeen C/12**	2.0	4.0	Product separated as an oil.
5-38-5	2.0	Ethomeen C/15**	2.0	4.0	" " " "
5-38-6	2.0	Ethomeen S/12**	2.0	4.0	" " " "
5-39-1	2.0	Propomeen HT/12**	2.0	4.0	No apparent change.
5-39-2	2.0	Propomeen C/25**	2.0	4.0	" " "
5-39-3	2.0	Menthane diamine***	2.0	4.0	Formed a dense stable suspension of fine particles.

*Manufactured by General Mills.
**Manufactured by Armour Industrial Chemical Company.
***Manufactured by Rohm and Haas.

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TABLE 2

GELATION OF JP-4 USING SEBACOYL CHLORIDE AND VARIOUS AMINES

Run No.	Wt % Acid Chloride	Amine	Wt % Amine	Wt % Total Additives	Remarks
5-39-4	1.5	Alamine 21D* (Coco amine)	1.5	3.0	Gradually formed viscoelastic gel. Viscosity increases with time.
5-39-5	0.3	Alamine 21D* (Coco amine)	0.7	1.0	Gradually formed viscoelastic gel. Viscosity increases with time.
5-39-6	2.0	Alamine 4D* (Lauryl amine)	2.0	4.0	Dense slurry of voluminous solids.
5-40-1	2.0	Diam 11* (N-Oleyl-1,3-propylene diamine)	2.0	4.0	Slight increase in viscosity. No gel.
5-40-2	2.0	Ethomeen C/12**	2.0	4.0	Product separated as an oil.
5-40-3	2.0	Ethomeen C/15**	2.0	4.0	" " " "
5-40-4	2.0	Ethomeen S/12**	2.0	4.0	" " " "
5-40-5	2.0	Propomeen HT/12**	2.0	4.0	No apparent change.
5-40-6	2.0	Propomeen C/25**	2.0	4.0	" " "
5-40-7	1.0	Menthane diamine***	2.0	3.0	Formed a stable suspension of fine particles.

*Manufactured by General Mills
**Manufactured by Armour Industrial Chemical Company.
***Manufactured by Rohm and Haas.

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TABLE 3

GELATION OF JP-4 USING DODECYL MALONYL CHLORIDE AND VARIOUS AMINES

Run No	Wt % Acid Chloride	Amine	Wt % Amine	Wt % Total Additives	Remarks
5-47 1	1 5	Alamine 21D* (Coco amine)	2 5	4 0	Formed a viscoelastic gel which improved on standing.
5-47 2	1 5	Alamine 4D* (Lauryl amine)	2.5	4.0	Formed a flocculent ppt.
5-47 3	1.5	Alamine 21D Alamine 4D	1.5 1.5	4.5	Formed a weak viscoelastic gel. Inferior to 5-47-1
5-47-4	1.5	Formonyte 605** (Tall oil amine)	2.5	4.0	Product soluble in JP-4.
5-47 5	1.5	Dimer diamine***	2.0	3.5	Formed a flocculent ppt
5 48 7	1.5	Formonyte 604** (Cottonseed amine)	1.5	3.0	Product soluble in JP-4 Only clouded the fuel.

*Manufactured by General Mills.
**Manufactured by Foremost Chemical Products Company
***Manufactured by Emery Industries.

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TABLE 4

GELATION OF JP-4 USING OCTYL MALONYL CHLORIDE AND VARIOUS AMINES

Run No	Wt % Acid Chloride	Amine	Wt % Amine	Wt % Total Additives	Remarks
6-6-1	1.8	Alamine 4D (Lauryl amine)	2 7	4.5	Formed a fine ppt
6-6-2	1.3	Alamine 21D (Coco amine)	3 3	4.6	Formed a viscoelastic gel which improved on standing.
6-6-3	1.8	Menthane diamine	2.4	4.2	Formed a ppt which immediately settled.
6-7-4	1.3	Formonyte 605 (Tall oil amine)	2.5	3.8	Product soluble in JP-4.
6-7-5	1.3	Formonyte 604 (Cottonseed amine)	2.5	3.8	Product soluble in JP-4 Only clouded the fuel.
6-7-6	1.3	Formonyte 608 (Oleyl amine)	2.8	4.1	Product soluble in JP-4
6-7-7	1.3	Dimer diamine	3.0	4.3	Formed a sticky ppt which agglomerated

TABLE 5

GELATION OF JP-4 USING DODECYL MALONYL CHLORIDE WITH PRIMARY AND TERTIARY AMINES

Run No.	Wt % Acid Chloride	Primary Amine	Wt % Primary Amine	Tertiary Amine	Wt % Tertiary Amine	Wt % Total Additives	Remarks
6-24-1	1.5	Alamine 21D* (Coco amine)	2.5	Pyridine	0.7	4.7	Formed a viscoelastic gel.
6-24-2	1.5	Alamine 4D* (Lauryl amine)	2.5	Pyridine	0.7	4.7	Formed a flocculent ppt.
6-24-4	1.5	Formmyte 605** (Tall oil amine)	2.5	Pyridine	0.7	4.7	Soluble in JP-4.
6-25-5	1.5	Alamine 21D (Coco amine)	2.5	Tributyl amine	1.8	5.8	Formed a viscoelastic gel. Similar to 6-24-1.
6-25-6	1.5	"	2.5	N-methyl-morpholine	1.0	5.0	Formed a cloudy solution. Failed to gel JP-4.
6-25-7	1.5	"	2.5	Dimethyl formamide	0.7	4.7	Formed a visco-elastic gel. Similar to 6-24-1.
6-25-8	2.0	---	---	Tributyl amine	3.6	5.6	Formed a suspension of solids. When coco amine is added, a viscoelastic gel is formed.
6-25-9	2.0	---	---	N-methyl morpholine	2.0	4.0	Formed a ppt. When coco amine is added, the ppt. dissolves but no gel is obtained.

*Manufactured by General Mills.
**Manufactured by Foremost Chemical Products Company.

TABLE 6

GELATION OF JP-4 USING PHENYL DICHLOROPHOSPHATE AND VARIOUS AMINES

Run No	Wt % Acid Chloride	Amine	Wt % Amine	Wt % Total Additives	Remarks
6-10-1	1.8	Alamine 4D (Lauryl amine)	2.7	4.5	Formed a fine ppt which gradually settled.
6-10-2	1.3	Alamine 21D (Coco amine)	3.3	4.6	Formed a weak viscoelastic gel.
6-10-3	1.8	Menthane diamine	2.4	4.2	Formed a flocculent ppt
6-10-4	1.3	Formonyte 605 (Tall oil amine)	2 5	3.8	Soluble in JP-4
6-11-1	1.3	Formonyte 604 (Cottonseed amine)	2.5	3.8	Soluble in JP-4. Only clouded the fuel.
6-11-2	1.3	Formonyte 608 (Oleyl amine)	2 8	4.1	Soluble in JP-4.
6-11-3	1.3	Dimer diamine	3 0	4.3	Formed an oily ppt which agglomerated.

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TABLE 7

GELATION OF JP-4 USING p-TOLYL DICHLOROPHOSPHATE AND VARIOUS AMINES

Run No.	Wt % Acid Chloride	Amine	Wt % Amine	Wt % Total Additives	Remarks
6-14-1	1.8	Alamine 4D (Lauryl amine)	2.7	4.5	Formed a fine ppt.
6-14-2	1.3	Alamine 21D (Coco amine)	3.3	4.6	Formed a weak viscoelastic gel.
6-14-3	1.8	Menthane diamine	2.4	4.2	Formed a flocculent suspension
6-15-1	1.3	Formonyte 605 (Tall oil amine)	2.5	3.8	Soluble in fuel.
6-15-2	1.3	Formonyte 604 (Cottonseed amine)	2.5	3.8	Soluble in JP-4. Only clouded solution.
6-15-3	1.3	Formonyte 608 (Oleyl amine)	2.8	4.1	Soluble in JP-4.
6-15-4	1.3	Dimer diamine	3.0	4.3	Separated as an oil.

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TABLE 8

GELATION OF JP-4 USING CHLOROMETHYLPHOSPHONIC DICHLORIDE AND VARIOUS AMINES

Run No.	Wt % Acid Chloride	Amine	Wt % Amine	Wt % Total Additives	Remarks
6-12-1	1.8	Alamine 4D (Lauryl amine)	2.7	4.5	Formed a fine ppt which gradually settled.
6-12-2	1.3	Alamine 21D (Coco amine)	3.3	4.6	Formed a weak viscoelastic gel in 2 to 3 minutes
6-12-3	1.8	Menthane diamine	2.4	4.2	Formed a flocculent suspension.
6-13-1	1.3	Formonyte 605 (Tall oil amine)	2.5	3.8	Soluble in JP-4.
6-13-2	1.3	Formonyte 604 (Cottonseed amine)	2.5	3.8	Soluble in JP-4.
6-13-3	1.3	Formonyte 608 (Oleyl amine)	2.8	3.8	Soluble in JP-4.
6-13-4	1.3	Dimer diamine	3.0	4.3	Separated as an oil.

TABLE 9

EVALUATION OF 1-CHLORO-2, 4-BENZENE DIISOCYANATE AND VARIOUS AMINES

Run No.	Wt % Diisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
6-8-1	1.5	Alamine 4D (Lauryl amine)	2.7	4.2	Immediate product soluble. Formed ppt in 0.5 hour.
6-8-2	1.5	Alamine 21D (Coco amine)	3.0	4.5	Same as above.
6-8-3	1.5	Formamine 608 (Oleyl amine)	3.0	4.5	Soluble in JP-4.
6-8-4	1.5	Menthane diamine	2.4	3.9	Formed a voluminous ppt.
6-9-5	1.2	Dimer diamine	3.0	4.2	Formed a sticky ppt which agglomerated
6-9-10	1.5	Formamine 604 (Cottonseed amine)	3.0	4.5	Soluble in JP-4.
6-9-11	1.5	Formamine 605 (Tall oil amine)	2.5	4.0	Soluble in JP-4.
6-9-12	1.2	Formamine 801 (Coco diamine)	2.5	3.7	Formed a ppt.

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TABLE 10

GELATION OF JP-4 USING DECAMETHYLENE DIISOCYANATE AND VARIOUS AMINES

Run No	Wt % Diisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
5-49-1	1.2	Alamine 21D* (Coco amine)	1.8	3.0	Gelled JP-4 in 2-3 seconds. Gel was granular and fuel separated on standing
5-49-2	1.2	Alamine 4D (Lauryl amine)	1.8	3.0	Gelled JP-4 in 3 seconds. Gel was firmer than 5-49-1 but fuel separated on standing.
5-49-3	1.2	Formonyte 608*** (Oleyl amine)	2.8	4.0	Gelled JP-4 in 1-2 seconds. A good gel was obtained. It was weaker than Hylene TM-65 - lauryl amine gel.
5-49-4	1.2	Menthane diamine**	1.8	3.0	Formed a flocculent ppt.
5-49-5	1.2	Diam 11* (N-Oleyl-1,3-propylene diamine)	2.8	4.0	Soluble in JP-4.
5-49-6	1.2	Diam 21* (N-Coco-1,3-propylene diamine)	2.2	3.4	Separated as an oil.

*Manufactured by General Mills.
**Manufactured by Rohm and Haas
***Manufactured by Foremost Chemical Products Company

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TABLE 11

GELATION OF JP-4 USING HEXAMETHYLENE DIISOCYANATE AND VARIOUS AMINES

Run No.	Wt % Diisocyanate	Amine	Wt % Amine	Wt % Total Additives	°C JP-4	Remarks
6-2-1	1.2	Formonyte 608* (Oleyl amine)	2.8	4.0	25	Rapidly formed a firm gel Gel superior to one obtained with Hylene TM-65-lauryl amine.
6-2-1A	"	"	"	"	0	Same as above.
6-2-2	1.2	Alamine 11D** (Oleyl amine)	2.8	4.0	0	Same as above.
6-2-5	1.2	Formonyte 608	2.8	4.0	-10	Rapidly gelled JP-4. Gel somewhat weaker than 6-2-1. This is considered lower temperature limit.
6-3-3	1.0	Alamine 4D (Lauryl amine)	1.8	2.8	24	Formed a firm gel. Reaction extremely fast. Gel not as firm as 6-2-1.
6-3-3A	"	"	"	"	0	Did not form a gel because amine is not soluble in JP-4 at 0°.

*Manufactured by Foremost Chemical Products Company.
**Manufactured by General Mills.

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TABLE 12

GELATION OF JP-4 USING TETRAMETHYLENE DIISOCYANATE AND VARIOUS AMINES

Run No.	Wt % Diisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
6-26-1	1.0	Oleyl amine	2.8	3.8	Formed a weak gel. Gel inferior to one obtained using hexamethylene diisocyanate.
6-26-2	2.0	Butyl amine	2.0	4.0	Too soluble. Formed a "slush".
6-26-3	1.8	Hexyl amine	2.2	4.0	Reaction rate extremely fast. Unable to obtain good mixing. Product formed a good gel but fuel rapidly exudes.
6-26-4	1.0	Primene JM-T*	2.8	3.8	Soluble in JP-4.
6-29-2	2.1	Isopropyl amine	1.7	3.8	Formed a weak particulate gel.
6-31-3	1.0	Lauryl amine	3.0	4.0	Formed a weak grainy gel. Gel particulate and displayed syneresis.
6-31-2	1.0	Coco amine	3.0	4.0	Formed a weak grainy gel. Gel displayed syneresis.
6-31-4	1.2	Amine 803**	2.8	4.0	Formed a viscoelastic gel. Product inferior to that obtained with hexamethylene diisocyanate.
6-30-1	1.9	Amine 803 Hexyl amine	1.9 0.6	4.4	Formed a gel very rapidly. Could not obtain good mixing. Formed a good gel but was not viscoelastic.

*Manufactured by Rohm & Haas.

**2-Ethylhexyl-3-aminopropyl ether manufactured by Union Carbide.

TABLE 13

EVALUATION OF AMINE 803* WITH VARIOUS DIISOCYANATES

Run No.	Wt % Amine	Diisocyanate	Wt % Diisocyanate	Wt % Total Additives	Remarks
6-27-1	2.7	Hylene TM-65**	1.3	4.0	Formed a thick gel. Not rigid and appeared to approach viscoelasticity.
6-27-2	2.8	Hexamethylene diisocyanate	1.2	4.0	Formed a tough viscoelastic gel.
6-27-3	1.4	"	0.6	2.0	Similar to 6-27-2 but somewhat weaker.
6-27-4	0.7	"	0.3	1.0	Formed a weak viscoelastic gel.

*2-Ethylhexyl-3-aminopropyl ether manufactured by Union Carbide.
**Manufactured by Du Pont.

TABLE 14

GELATION OF JP-4 USING 4-METHOXY-m-PHENYLENE DIISOCYANATE* AND VARIOUS AMINES

Run No.	Wt % Diisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
6-34-1	1.5	Coco amine	2.7	4.2	Formed a thick viscoelastic gel. Reaction too slow to be practical. Run in hot JP-4 in order to increase solubility of diisocyanate in JP-4.
6-34-2	2.0	Hexyl amine	2.0	4.0	Formed a thick grainy gel. Reaction too slow. Run in hot JP-4.
6-34-3	1.5	2-Ethylhexyl-3-aminopropyl ether	2.7	4.2	Formed a strong viscoelastic gel. Reaction too slow to be practical. Reaction run in hot JP-4 in order to increase solubility of diisocyanate.

*Because of low solubility of diisocyanate, it was necessary to heat the JP-4.

TABLE 15

GELATION OF JP-4 USING THE DIMER OF 1,3,5-BENZENE TRIISOCYANATE AND VARIOUS AMINES

Run No	Wt % Triisccyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
6-35-1	1.5	2 Ethylhexyl-3-aminopropyl ether	2.7	4.2	It was necessary to heat the JP-4 in order to dissolve the triisocyanate. A tough gel was obtained after about 1 hour at 65°C. On cooling, a good dilatant gel was obtained.
6-35-2	3.0	Hexyl amine	2.0	5.0	A particulate gel was obtained. It was necessary to heat the JP-4 in order to dissolve the triisocyanate.
6-35-3	1.5	Coco amine	2.7	4.2	A particulate gel was obtained. This gel was more rigid than was obtained in Run No. 6-35-2.

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TABLE 16

GELATION OF JP-4 USING THE DIMER OF 2, 4, 6-TOLUENE TRIISOCYANATE AND VARIOUS AMINES

Run No.	Wt % Triisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
6-36-1	1.5	2-Ethylhexyl-3-aminopropyl ether	2.7	4.2	Necessary to heat the JP-4 in order to dissolve the triisocyanate. A very tough gel is obtained. Actually gel is dilatant. This is the best gel prepared to date.
6-36-2	1.5	Coco amine	2.7	4.2	The results are similar to above except that gel is somewhat weaker.
6-36-3	3.0	Hexyl amine	2.0	5.0	Necessary to heat the JP-4 in order to dissolve the triisocyanate. On cooling, the product formed swollen lumps of solids suspended in free fuel

TABLE 17

GELATION OF JP-4 USING 2, 4, 6-TOLUENE TRIISOCYANATE AND VARIOUS AMINES

Run No.	Wt % Triisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
7-7-1	1.5	2-Ethylhexyl amine	2.5	4.0	It was necessary to melt the triisocyanate in order to obtain rapid dissolution in the JP-4. This system immediately formed a dilatant gel. The gel was tough and dry. One of the best prepared to date.
7-7-2	1.0	Coco amine	3.0	4.0	This system immediately formed a gel. Properties of this gel are the same as obtained above.
7-7-3	1.0	2-Ethylhexyl-3-aminopropyl ether	2.6	3.6	Immediately formed a dilatant gel. This gel was not as rigid as obtained above.
7-7-4	1.5	1,1,3,3-Tetramethyl butyl amine	2.5	4.0	This system formed a thick slurry of solids in the JP-4.

TABLE 18

EVALUATION OF 2, 4, 6-TOLUENE TRIISOCYANATE SOLUTIONS WITH VARIOUS AMINES AS JP-4 GELLANTS

Run No.	Amine	Wt % Amine	Isocyanate	Wt % Isocyanate	Wt % Total Additives	Remarks
7-10-1	2-Ethylhexylamine	2.6	TTI* HDI**	0.7	4.0	This system slowly thickened the fuel and after approximately 1 minute it formed a dilatant gel.
7-10-2	Coco amine	2.7	TTI HDI	0.65 0.65	4.0	Same as above.
7-10-3	Hexyl amine	2.0	TTI HDI	0.75 0.75	3.5	Same as above.
7-10-4	2-Ethylhexylamine	2.6	TTI Hylene TM-65	0.7 0.7	4.0	Slightly increased the viscosity of the fuel.
7-10-5	Coco amine	2.6	TTI Hylene TM-65	0.7 0.7	4.0	Same as above.
7-10-6	1,1,3,3-Tetramethyl butyl amine	2.7	TTI Hylene TM-65	0.65 0.65	4.0	Formed a swollen ppt in in the JP-4.

*2,4,6-Toluene triisocyanate

**Hexamethylene diisocyanate

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TABLE 19

GELATION OF JP-4 USING 1, 3, 5-BENZENE TRIISOCYANATE AND PRIMARY AMINES

Run No.	Wt % Triisocyanate	Amine	Wt % Amine	Wt % Total Additives	°C	Remarks
7-11-3	1.4	Coco amine	2.6	4.0	25	This system required approximately 30 minutes to gel the fuel.
7-11-4	1.4	Coco amine	2.6	4.0	65	Same as above
7-12-1	2.0	2-Ethylhexylamine	2.0	4.0	25	This system required about 1.5 hrs. to gel the fuel.
7-12-2	2.0	2-Ethylhexylamine	2.0	4.0	65	Formed a gel in approximately 2 minutes.

TABLE 20

GELATION OF JP-4 USING p-XYLYLENE DIISOCYANATE AND VARIOUS AMINES

Run No.	Wt % Diisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
7-19-1	1.0	Coco amine	2.0	3.0	Reaction is very rapid. Product formed a swollen suspension of solids.
7-19-2	1.0	Oleyl amine	2.0	3.0	This system rapidly gelled the fuel. The gel was soft and easily broken.
7-19-3	0.9	t-Octyl amine	1.1	2.0	Formed a ppt. in JP-4
7-19-4	0.9	Hexyl amine	1.1	2.0	Formed a suspension of gelatinous solids.
7-19-5	1.0	2-Ethylhexylamine	2.0	3.0	This system slowly gelled the fuel. It required about 10 minutes for forming a particulate gel.
7-19-6	1.0	2-Ethylhexyl-3-amino propyl ether	1.6	2.6	Rate of reaction is too fast to obtain good mixing. Product formed a tough visco-elastic gel.
7-19-7	0.9	m-Xylylene diamine	1.6	2.5	Formed a ppt. in the fuel.
7-19-8	0.9	o-Xylylene diamine	1.6	2.5	Formed a ppt. in the fuel.

TABLE 21

GELATION OF JP-4 USING m-PHENYLENE DIISOCYANATE AND VARIOUS AMINES

Run No.	Wt % Diisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
7-23-1	0.8	Oleyl amine	2.8	3.6	This system required approximately 2 minutes to form a weak thixotropic gel.
7-23-2	0.8	Lauryl amine	1.8	2.6	Immediately formed a weak, grainy particulate gel. Gel easily broken.
7-23-3	0.8	Coco amine	2.4	3.2	Same as above.
7-23-4	0.8	2-Ethylhexylamine	1.4	2.2	This system formed a ppt. in JP-4. The ppt. agglomerated.
7-23-5	0.8	2-Ethylhexyl-3-amino-propyl ether (Amine 803)	1.8	2.6	This system required approximately 10 minutes to form a tough viscoelastic gel.
7-23-6	1.6	Hexyl amine	2.0	3.6	Product formed a suspension of highly swollen solids.
7-23-7	0.8	t-octyl amine	1.4	2.2	This system slowly formed a suspension of swollen solids.
7-24-2	2.0	Menthane diamine	2.0	4.0	Product formed a ppt. in JP-4.

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TABLE 22

GELATION OF JP-4 USING m-XYLYLENE DIISOCYANATE AND VARIOUS AMINES

Run No.	Wt % Diisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
7-50-1	1.7	4-Chlorobenzyl amine	2.3	4.0	Instantaneously formed a very firm particulate gel. Some free fuel. Probably poor mixing.
7-50 2	0.85	4-Chlorobenzyl amine	1.15	2.0	Instantaneously formed a very firm particulate gel. Some free fuel. Gel same as above.
8-1-1	0.4	4-Chlorobenzyl amine	0.6	1.0	Instantaneously formed a very firm particulate gel. Some syneresis. Gel about as firm as above.
8-1-3	0.9	Delta aminobutylmethyl diethoxysilane	2.1	3.0	Product soluble.
8-5-1	1.0	Oleyl amine	3.0	4.0	Formed a weak gel. Gel was thixotropic. Required 6 to 10 seconds to gel.
8-5-2	0.9	Dimer diamine	3.1	4.0	Formed a voluminous suspension of solids. Required about 5 seconds to gel.
8-5-3	1.35	Lauryl amine	2.65	4.0	Instantaneously formed a very dry particulate gel.
8-5-4	1.4	Menthane diamine	2.6	4.0	Formed voluminous suspension of solids.

TABLE 22 (Cont'd)

Run No.	Wt % Diisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
8-6-1	1.6	p-Phenetidine	2.4	4.0	Formed a very dry particulate gel in approximately 1 minute.
8-6-2	1.0	Tall oil amine	3.0	4.0	Formed a good thixotropic gel. Required about 5 seconds to gel.
8-6-3	1.7	2-Ethylhexylamine	2.3	4.0	Product soluble.
8-6-4	1.6	o-Phenetidine	2.4	4.0	Slowly formed a ppt.
8-7-1	1.9	o-Toluidine	2.1	4.0	Required about 5 minutes to form a very dry hard particulate gel.
8-13-1	1.35	Amine 803	2.65	4.0	Formed a tough viscoelastic gel. Required about 10 minutes to gel.

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TABLE 23

GELATION OF JP-4 USING 4, 6-DIMETHYL-1, 3-XYLYLENE DIISOCYANATE AND VARIOUS AMINES

Run No.	Wt % Diisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
8-28-1	2.0	4-Chlorobenzylamine	2.5	4.5	Instantaneously forms a dry particulate gel. Gel has greater cohesive strength than does the one obtained with xylylene diisocyanate and the same amine.
8-28-2	2.4	p-Ethyl aniline	2.2	4.6	Slowly formed a weak, grainy gel.
8-28-3	2.0	o-Toluidine	2.0	4.0	Slowly formed a weak, grainy gel.
8-29-1	1.8	Amine 803	2.4	4.2	Immediately formed a good particulate gel.
8-29-2	2.2	Menthane diamine	3.4	5.6	Rapidly formed a thick slurry of solids.
8-29-3	1.5	Lauryl amine	2.5	4.0	Instantaneously formed a good gel.
8-29-4	2.0	p-Phenetidine	2.4	4.4	Rapidly formed a dry particulate gel.
8-30-1	1.0	Dimer diamine	3.0	4.0	Rapidly formed a thick slurry of solids.
8-30-2	2.0	3-Aminomethyl pyridine	2.0	4.0	Product formed a ppt. in JP-4.
8-30-3	2.2	t-Isopropylbenzylamine	3.0	5.2	Instantaneously formed a dry particulate gel. Gel had little cohesive strength

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TABLE 23 (Cont'd)

Run No.	Wt % Diisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
8-30-4	2 0	Ethoxyethylamine	2.0	4.0	Instantaneously formed a dry particulate gel.
8-31-1	2.0	Dodecenyl-3-aminopropyl ether	3.4	5.4	Slowly formed a viscoelastic gel
8-31-2	2.0	Aniline	2.0	4.0	Slowly formed a dry particulate gel.
8-31-3	2.2	n-Hexylamine	2.0	4.2	Rate of gelation too fast to obtain good mixing. Formed a particulate gel.
8-31-4	2.0	n-Coco-1,3-propylene diamine	3.0	5.0	Product separated from JP-4 as an oil.
8-31-5	2.0	2-Ethylhexylamine	2.0	4.0	Formed a weak viscoelastic gel.
8-32-1	1.2	Oleyl amine	2.8	4.0	Product formed a clear tough gel.
8-32-2	2.2	t-Octylamine	2.6	4.8	Product soluble in fuel.
8-32-3	2.2	"Delta" silane	2.4	4.6	Instantaneously formed a good particulate gel.
8-32-4	2.2	1,4-Bis(isocyanatomethyl) cyclohexane	1.8	4.0	Product formed a ppt. in JP-4.

TABLE 24

GELATION OF JP-4 USING 1, 4-BIS(ISOCYANATOMETHYL) CYCLOHEXANE AND VARIOUS AMINES

Run No.	Wt % Diisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
7-24-3	1.0	Oleyl amine	2.8	3.8	This system formed a weak, grainy particulate gel in 3 to 5 seconds.
7-24-4	1.0	Lauryl amine	1.8	2.8	This system merely increased the viscosity of the fuel.
7-24-5	0.8	Coco amine	2.4	3.2	Slowly formed a weak grainy gel.
7-24-6	2.0	2-Ethylhexylamine	2.6	4.6	Required several minutes to form a weak dilatent gel.
7-25-2	2.0	Hexyl amine	2.0	4.0	Immediately formed a weak particulate gel.
7-25-3	2.0	Amine 803	3.6	5.6	Required approximately 3 minutes to form a tough viscoelastic gel.
7-25-5	1.0	Menthane diamine	1.6	2.6	Immediately formed a suspension of voluminous solids.
7-25-6	1.0	t-Octyl amine	2.8	3.8	Immediately formed a weak particulate gel.
7-25-7	2.2	1,4-Bis(aminomethyl) cyclohexane	2.2	4.4	Formed a ppt. in JP-4.

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TABLE 25

GELATION OF JP-4 USING MENTHANE DIISOCYANATE AND VARIOUS AMINES

Run No.	Wt % Diisocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
7-31-1	1.1	Oleyl amine	2.8	3.9	Formed a weak gel. This system required approximately 5 minutes to gel JP-4.
7-31-2	1.25	Lauryl amine	2.4	3.65	Formed a gel somewhat firmer than above. This gel had a consistency of grease. Approximately 4 minutes were required to gel the fuel.
7-31-3	1.8	Hexyl amine	1.75	3.55	Converted JP-4 into a weak gel about 5 minutes after additives were added to fuel.
7-31-4	1.8	2-Ethylhexylamine	2.0	3.8	Converted fuel to a weak gel. System slower than run no. 7-31-3.
7-31-5	1.9	Menthane diamine	2.1	4.0	This system slowly formed a ppt. in JP-4.
7-32-1	1.5	t-Octyl amine	2.0	3.5	Slowly formed a ppt. in JP-4.
7-32-2	1.5	Dimer diamine	2.5	4.0	Slowly formed a ppt. in JP-4.
7-32-3	1.7	N-Coco-1,3-propylene diamine	2.3	4.0	Slowly formed a ppt which agglomerated.
7-32-4	1.5	N-Oleyl-1,3-propylene diamine	2.5	4.0	This system formed a weak particulate gel. Rate of gelation faster than obtained above.

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TABLE 26

GELATION OF JP-4 USING OLEYL ISOCYANATE AND VARIOUS AMINES

Run No.	Wt % Isocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
7-35-1	2.95	Menthane diamine	1.05	4.0	Formed a clear thin gel in approximately 1.5 minutes. Product similar to one obtained using menthane diisocyanate and oleyl amine.
7-35-2	3.0	1,4-Bis(aminomethyl) cyclohexane	0.7	3.7	Product formed a weak grainy gel in 1 to 2 seconds.
7-35-3	2.9	Coco amine	2.0	4.9	Product thickened the fuel but failed to form a gel.
7-35-4	2.5	N-Coco-1,3-propylene diamine	2.5	5.0	Product soluble in JP-4.
7-35-5	2.5	Rosin amine	2.5	5.0	Product soluble in JP-4.
7-36-1	3.5	Trimethyle .e diamine	0.5	4.0	This system rapidly converted JP-4 into a particulate gel. Gel was weak and easily broken.
7-36-2	3.0	Tetraethylene pentamine	1.0	4.0	Product soluble in JP-4.
7-36-3	3.0	Cyclohexylamine	1.0	4.0	Product soluble in JP-4.
7-36-4	3.0	Hexyl amine	1.0	4.0	Product soluble in JP-4.

TABLE 27

GELATION OF JP-4 USING 3-CHLOROPHENYL ISOCYANATE AND VARIOUS AMINES

Run No.	Wt % Isocyanate	Amine	Wt % Amine	Wt, % Total Additives	Remarks
7-41-1	1.38	Oleyl amine	2.62	4.0	Product soluble in JP-4
7-41-2	1.4	Coco amine	2.6	4.0	Product soluble in JP-4.
7-41-3	1.8	Lauryl amine	2.2	4.0	Slowly formed a grainy ppt.
7-41-4	2.4	n-Hexyl amine	1.6	4.0	Product soluble in JP-4
7-42-1	2.2	2-Ethylhexyl amine	1.8	4.0	Product soluble in JP-4
7-42-2	2.4	Cyclohexyl amine	1.6	4.0	Slowly formed a voluminous ppt
7-42-3	2.0	Amine 803	2.0	4.0	Soluble product.
7-42-4	2.2	t-Octyl amine	1.8	4.0	Soluble product
7-42-5	2.2	3-Aminomethyl pyridine	1.8	4.0	Formed a gummy ppt.
7-43-1	2.2	4-Chlorobenzyl amine	1.8	4.0	Formed a very firm cake-like gel. Gelation rate is extremely fast.
7-43-3	2.55	Menthane diamine	1.45	4.0	Formed a ppt. instantaneously.
7-44-1	1.4	1,4-Bis(aminomethyl) cyclohexane	2.6	4.0	Formed a ppt. instantaneously.
7-46-4	0.75	4-Chlorobenzyl amine	1.25	2.0	Formed a very firm cake like gel. About the same as 7-43-1. Rate extremely fast.

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TABLE 28

GELATION OF JP-4 USING NAPHTHYL ISOCYANATE AND VARIOUS AMINES

Run No.	Wt % Isocyanate	Amine	Wt % Amine	Wt % Total Additives	Remarks
8-38-2	1.7	n-Coco-1, 3-propylene diamine	2.5	4.2	Product formed a ppt. in JP-4.
8-38-3	1.7	Lauryl amine	1.8	3.5	Required about 5 seconds to form a firm particulate gel.
8-38-4	1.7	Oleyl amine	2.8	4.5	Product soluble in the fuel.
8-38-5	1.7	Tall oil amine	2.5	4.2	Product soluble in JP-4.
8-38-6	1.7	2-Ethylhexylamine	1.8	3.5	Product soluble in JP-4.
8-39-1	1.7	Cyclohexylamine	1.0	2.7	Formed a voluminous ppt. in the fuel.
8-39-2	2.0	Ethoxyethylamine	1.0	3.0	Immediately forms a firm particulate gel. When compressed the fuel exudes.
8-39-3	2.0	Menthane diamine	1.0	3.0	Immediately formed a ppt. in JP-4.
8-39-4	2.0	Dimer diamine	2.0	4.0	Immediately formed a ppt. which agglomerated.
8-39-5	1.7	Coco amine	2.2	3.9	Required about 5 seconds to gel the fuel.

TABLE 29

GELATION OF JP-4 USING 1, 1, 3, 3-TETRAMETHYL BUTYL AMINE AND VARIOUS ISOCYANATES

Run No.	Wt % Amine	Isocyanate	Wt % Isocyanate	Wt % Total Additives	Remarks
6-48-1	2.6	Hexamethylene diisocyanate	1.7	4.3	Product was soluble in JP-4.
6-48-2	2.6	Hylene TM-65	1.7	4.3	Gelled JP-4. The gel was similar to the one obtained with Hylene TM-65 and lauryl amine but rate was somewhat slower.
7-9-1	2.5	1-chloro, 2, 4-benzene diisocyanate	1.5	4.0	Product slightly increased the viscosity of the fuel.
7-9-2	2.7	2, 6-Tolylene diisocyanate	1.3	4.0	Product formed a ppt. after approximately 1 minute.
7-9-3	2.3	2, 4, 6-Toluene triisocyanate	1.7	4.0	It was necessary to heat the triisocyanate before addition. Product formed a ppt.
7-9-4	2.4	4-Methoxy-m-phenylene diisocyanate	1.6	4.0	Product formed a ppt. in JP-4.
7-9-5	2.7	2, 4-Tolylene diisocyanate	1.3	4.0	Product soluble in JP-4.

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TABLE 30

ATTEMPTED GELATION OF JP-4 USING 2-ETHYLHEXYL AMINE AND VARIOUS DIISOCYANATES

Run No.	Wt % Amine	Diisocyanate	Wt % Diisocyanate	Wt % Total Additives	Remarks
7-6-1	2.5	Hylene TM - 65	1.5	4.0	This system required approximately 2 minutes to convert the fuel to a weak gel.
7-6-2	2.5	Hexamethylene diisocyanate	1.5	4.0	Formed a ppt. that rapidly agglomerates.
7-6-3	2.5	2,6-Tolylene diisocyanate	1.5	4.0	Immediately formed a dispersion of gelatinous solid.

TABLE 31

ATTEMPTED GELATION OF JP-4 USING DIETHYLAMINOPROPYLAMINE AND VARIOUS ISOCYANATES AND DIISOCYANATES

Run No.	Wt % Amine	Isocyanate	Wt % Isocyanate	Wt % Total Additives	Remarks
8-35-1	2.6	Hylene TM-65	1.6	4.2	Immediately formed a thixotropic slurry of solids.
8-35-2	2.6	Menthane diisocyanate	2.2	4.8	Formed a ppt. in JP-4.
8-36-1	2.6	m-Xylylene diisocyanate	2.2	4.8	Formed a thixotropic slurry of solids.
8-36-2	2.6	Hexamethylene diisocyanate	1.8	4.4	Immediately formed a dry particulate gel with very little cohesive strength.
8-36-3	2.6	1,4-Bis(isocyanatomethyl) cyclohexane	2.0	4.6	Formed a ppt. in JP-4.
8-36-4	2.6	m-Tolyl isocyanate	1.6	4.2	Product soluble in JP-4.
8-37-4	2.0	Oleyl isocyanate	2.0	4.0	Product soluble in JP-4.
8-37-5	2.0	Naphthyl isocyanate	2.0	4.0	Formed a ppt. in JP-4.

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TABLE 32

EVALUATION OF N, N-BIS(AMINOBUTYL) BENZYLAMINE AND
VARIOUS ISOCYANATES AS FUEL GELLANTS

Run No.	Wt % Amine	Isocyanate	Wt % Isocyanate	Wt % Total Additives	Remarks
7-12-3	2.0	Hylene TM-65 (tolylene diisocyanate)	2.0	4.0	Formed a ppt.
7-12-4	2.0	Hexamethylene diisocyanate	2.0	4.0	Formed a ppt
7-12-5	2.0	m-Tolyl Isocyanate	2.0	4.0	Formed a suspension of gelatinous solids.

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TABLE 33

ATTEMPTED GELATION OF JP-4 USING CYCLOHEXYLAMINE AND VARIOUS DIISOCYANATES

Run No.	Wt % Amine	Diisocyanate	Wt % Diisocyanate	Wt % Total Additives	Remarks
7-37-1	2.0	Hylene TM-65	1.75	3.75	Product formed a thick suspension of solids.
7-37-2	2.0	2,4-Tolylene diisocyanate	1.75	3.75	Product formed a thick suspension of solids.
7-37-3	2.0	Hexamethylene diisocyanate	1.7	3.7	Product formed a weak grainy gel in JP-4.
7-37-4	2.1	1,4-Bis(isocyanatomethyl) cyclohexane	1.9	4.0	Formed a ppt. in JP-4.
7-37-5	2.1	Menthane diisocyanate	2.0	4.1	Product formed a ppt. in JP-4.

TABLE 34

ATTEMPTED GELATION OF JP-4 USING 1, 4-BIS(AMINOMETHYL) CYCLOHEXANE AND VARIOUS ISOCYANATES

Run No.	Wt % Diamine	Isocyanate	Wt % Isocyanate	Wt % Total Additives	Remarks
7-21-1	1.0	Hylene TM-65 (tolylene diisocyanate)	1.0	2.0	Product formed a ppt. in JP-4
7-21-2	1.0	Hexamethylene diisocyanate	1.0	2.0	Same as above.
7-21-3	1.0	m-Tolyl isocyanate	1.0	2.0	Same as above.
7-24-1	2.0	m-Phenylene diisocyanate	2.0	4.0	Product formed a ppt. in JP-4.

TABLE 35

GELATION OF JP-4 USING 3-AMINOMETHYL PYRIDINE AND VARIOUS DIISOCYANATES

Run No	Wt % Amine	Diisocyanate	Wt % Diisocyanate	Wt % Total Additives	Remarks
7-44-2	2.2	Hylene TM-65	1.8	4.0	Formed a very dense suspension of solids. Rate was extremely fast
7-44-3	2.0	Menthane diisocyanate	2.0	4.0	Immediately formed a heavy dense ppt.
7-44-4	2.2	1,4- Bis(isocyanatomethyl) cyclohexane	1.8	4.0	Immediately formed a ppt.
7-45-1	2.3	Hexamethylene diisocyanate	1.7	4.0	Immediately formed a ppt.
7-45-2	1.0	Oleyl isocyanate	3.0	4.0	Slowly formed a weak, thick slurry.

TABLE 36

JP-4 GELATION USING ANILINE AND VARIOUS ISOCYANATES AND DIISOCYANATES

Run No.	Wt % Amine	Isocyanate	Wt % Isocyanate	Wt % Total Additives	Remarks
8-8-1	1.7	m-Tolyl isocyanate	2.3	4.0	Formed a very dry particulate gel in about 5 minutes.
8-8-2	1.7	p-Tolyl isocyanate	2.3	4.0	Formed a ppt.
8-8-3	1.8	Phenyl isocyanate	2.2	4.0	Formed a suspension of swollen solids
8-8-4	1.5	3-Chlorophenyl isocyanate	2.5	4.0	Same as 8-8-3
8-8-6	1.4	m-Xylylene diisocyanate	2.6	4.0	Formed a firm dry cake after about 2 minutes.
8-8-7	2.2	Tetramethylene diisocyanate	1.8	4.0	Formed a flocculent suspension.
8-9-1	2.1	2,4-Tolylene diisocyanate	1.9	4.0	Required 5 minutes to form a weak particulate gel.
8-9-2	2.0	1,4-Bis(isocyanatomethyl) cyclohexane	2.0	4.0	Same as 8-9-1
8-9-3	2.0	Hylene TM-65	2.0	4.0	Formed a voluminous ppt.

TABLE 37

GELATION OF JP-4 USING 0-TOLUIDINE AND VARIOUS ISOCYANATES OR DIISOCYANATES

Run No.	Wt % Amine	Isocyanate	Wt % Diisocyanates	Wt % Total Additives	Remarks
7-49-1	2.2	m-Xylylene diisocyanate	1.8	4.0	Slowly formed a very dry particulate gel.
7-49-2	2.3	Hylene TM-65	1.7	4.0	Slowly formed a weak gel.
7-49-3	2.4	Menthane diisocyanate	1.6	4.0	Slowly formed a ppt.
7-49-4	1.0	Oleyl isocyanate	3.0	4.0	Product soluble in JP-4.
7-48-5	1.6	' Chlorophenyl isocyanate	2.4	4.0	Slowly formed a very dry particulate gel.
7-50-1	2.2	Hexamethylene diisocyanate	1.8	4.0	Slowly formed a very thick suspension of solids.

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TABLE 38

JP-4 GELATION USING 4-CHLOROBENZYLAMINE AND VARIOUS DIISOCYANATES

Run No.	Wt % Amine	Diisocyanate	Wt % Diisocyanate	Wt % Total Additives	Remarks
8 3-4	2.4	Hylene TM-65	1.6	4.0	Instantaneously formed a weak grainy gel. Some free fuel.
8 4-1	2.4	Hexamethylene diisocyanate	1.6	4.0	Rapidly formed a weak grainy gel.
8-4-2	2.1	Menthane diisocyanate	1.9	4.0	Formed a ppt which agglomerated.
8-4-3	2.3	1,4 Bis(isocyanatomethyl) cyclohexane	1.7	4.0	Formed a thick slurry of solids.
8-4-4	1.25	Oleyl isocyanate	3.0	4.25	Formed a ppt

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TABLE 39

ATTEMPTED GELATION OF JP-4 USING 2, 4-DICHLOROBENZYLAMINE AND ISOCYANATES OR DIISOCYANATES

Run No.	Wt % Amine	Isocyanate	Wt % Isocyanate	Wt % Total Additives	Remarks
8-17-3	2.6	m-Xylylene diisocyanate	1.4	4.0	Formed a thick suspension of solids.
8-18-1	2.7	Hylene TM-65	1.3	4.0	Formed a thin slurry of solids.
8-18-2	2.5	Hexamethylene diisocyanate	1.5	4.0	Product insoluble in JP-4.
8-18-3	2.45	Menthane diisocyanate	1.55	4.0	Product formed a ppt. in JP-4
8-18-4	2.7	Chlorophenyl isocyanate	1.3	4.0	Product formed a ppt. in JP-4.

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TABLE 40

SOLIDIFICATION OF JP-4 USING 4-ISOPROPYLBENZYLAMINE AND VARIOUS DIISOCYANATES

Run No.	Wt % Amine	Diisocyanate	Wt % Diisocyanate	Wt % Total Additives	Remarks
8-16-2	2.46	m-Xylylene diisocyanate	1.54	4.0	Rapidly formed a dry particulate gel Gel was grainy and could be easily broken
8-16-3	2.5	Hylene TM-65	1.5	4.0	Reaction product formed a thick slurry of solids.
8-16-4	2.3	Menthane diisocyanate	1.7	4.0	Product soluble in fuel
8-16-5	2.5	1,4-Bis(isocyanatomethyl) cyclohexane	1.5	4.0	Formed a thick suspension of solids
8-17-1	2.5	Hexamethylene diisocyanate	1.5	4.0	Rapidly converted the fuel to a grainy gel
8-17-2	2.7	m-Tolyl isocyanate	1.3	4.0	Required approximately 1 minute to form a weak gel

TABLE 41

GELATION OF JP-4 USING DODECENYL-2-AMINOETHYL ETHER AND VARIOUS DIISOCYANATES

Run No.	Wt % Amine	Diisocyanate	Wt % Diisocyanate	Wt % Total Additives	Remarks
7-27-1	2.25	Hylene TM-65	1.75	4.0	This system increased the viscosity of the fuel. No gel was obtained.
7-28-1	2.25	Hexamethylene diisocyanate	0.85	3.1	Rapidly converted JP-4 to a tough viscoelastic gel.
7-28-2	2.30	Tetramethylene diisocyanate	0.90	3.2	Rapidly converted JP-4 to a viscoelastic gel. The gel is weaker than the one obtained in Run No. 7-28-1.
7-29-1	2.44	1,4-Bis(isocyanatomethyl) cyclohexane	0.90	3.34	Converted the fuel to a tough viscoelastic gel. Rate of gelation is somewhat slow in that 6 to 7 seconds were required to gel the fuel.
7-29-2	3.2	2,4,6-Toluene triisocyanate	1.0	4.2	It was necessary to melt the triisocyanate before adding it to the fuel. This system slowly converted the fuel to a dilatant gel.
7-29-3	0.75	Hexamethylene diisocyanate	0.25	1.0	A good viscoelastic gel was obtained in approximately 6 seconds.

TABLE 42

JP-4 GELATION USING DELTA-AMINOBUTYLMETHYLDIETHOXYSILANE AND VARIOUS DIISOCYANATES

Run No.	Wt % Silane	Isocyanate	Wt % Isocyanate	Wt % Total Additives	Remarks
8-2-1	3.0	Menthane diisocyanate	1.0	4.0	Formed a good elastic gel. Required about 1 minute to gel.
8-2-3	2.75	m-Xylylene diisocyanate	1.25	4 0	Product soluble.
0-2-2	2.8	Hylene TM-65	1.2	4.0	Rapidly formed a weak particulate gel.
8-2-4	2.4	Hexamethylene diisocyanate	1.6	4.0	Rapidly formed a tough visco-elastic gel.
8-2-5	2.75	1,4-Bis(isocyanatomethyl) cyclohexane	1.25	4.0	Formed a ppt. in the fuel.
8-3-1	2.8	2,6-Tolylene diisocyanate	1.2	4.0	Instantaneously formed a weak particulate gel.

TABLE 43

RATES OF GELATION USING VARIOUS GELLING AGENTS AT A TOTAL
ADDITIVE CONCENTRATION OF 4.0 WEIGHT PERCENT

Run No.	Additive System	Wt % Additive	Gelation Rate, Seconds
8-43-1	4-Chlorobenzylamine	2.3	0.2
	m-Xylylene diisocyanate	1.7	
8-43-2	β-Ethoxyethylamine	1.5	0.08
	Naphthyl isocyanate	2.5	
8-43-6	4-Chlorobenzylamine	2.2	0.06
	4,6-Dimethyl-1,3-xylylene diisocyanate	1.8	
8-44-6	Lauryl amine	2.5	0.08
	4,6-Dimethyl-1,3-xylylene diisocyanate	1.5	
8-43-3	β-Ethoxyethylamine	1.9	0.04
	4,6-Dimethyl-1,3-xylylene diisocyanate	2.1	
8-43-4	Oleyl amine	2.8	0.13
	4,6-Dimethyl-1,3-xylylene diisocyanate	1.2	
8-44-3	n-Hexylamine	2.3	0.05
	4,6-Dimethyl-1,3-xylylene diisocyanate	1.7	
8-44-4	4-Isopropylbenzylamine	2.3	0.10
	4,6-Dimethyl-1,3-xylylene diisocyanate	1.7	
8-44-7	Dodecenyl-2-aminoethyl ether	2.9	9.0
	1,4-Bis(isocyanatomethyl)cyclohexane	1.1	

TABLE 43 (Cont'd)

Run No.	Additive System	Wt % Additive	Gelation Rate, Seconds
8-41-1	Lauryl amine Hylene TM-65	2.7 1.3	1.5
8-41-2	Oleyl amine Hexamethylene diisocyanate	3.02 0.98	3.4
8-41-3	Amine 803 Hexamethylene diisocyanate	2.8 1.2	2.3
8-41-4	Dodecenyl-2-aminoethyl ether Hexamethylene diisocyanate	3.1 0.9	3.0
8-42-2	Lauryl amine Hexamethylene diisocyanate	2.5 1.5	1.1
8-42-3	"Delta" silane * Hexamethylene diisocyanate	2.4 1.6	1.9
8-42-4	Coco amine Naphthyl isocyanate	2.3 1.7	3.0

*Delta-aminobutylmethyldiethoxysilane.

TABLE 45 (Cont'd)

Run No.	Polyisocyanate		Amine		Wt % Total Additives	Remarks
	Name	Wt %	Name	Wt %		
6-39-4	Toluene triisocyanate	1.6	2-Ethylhexyl-3-aminopropyl ether	2.4	4.0	This is a dilatant gel. When placed on a transite board, it flowed over an area 6 inches in diameter and was approximately 0.5 inch thick. When ignited, the gel bubbled and released vapors of JP-4. It did not flow while burning.
6-41-1	4-Methoxy m-phenylene diisocyanate	1.3	2-Ethylhexyl-3-aminopropyl ether	2.7	4.0	The time of burning was 5 minutes. Once ignited, the gel exuded fuel which flowed over an area 15 to 18 inches in diameter.

TABLE 44 (Cont'd)

Run No.	Additive System	Wt % Additive	Gelation Rate, Seconds
8-42-6A	4-Chlorobenzylamine	1.35	0.07
	4,6-Dimethyl-1,3-xylylene diisocyanate	1.15	
8-42-7A	Lauryl amine	1.6	0.08
	4,6-Dimethyl-1,3-xylylene diisocyanate	0.9	
8-42-8A	β-Ethoxyethylamine	1.25	0.07
	4,6-Dimethyl-1,3-xylylene diisocyanate	1.25	
8-42-9A	Oleyl amine	1.75	0.13
	4,6-Dimethyl-1,3-xylylene diisocyanate	0.75	
8-44-3A	n-Hexyl amine	1.2	0.45
	4,6-Dimethyl-1,3-xylylene diisocyanate	1.3	
8-44-4A	4-Isopropylbenzylamine	1.25	0.16
	4,6-Dimethyl-1,3-xylylene diisocyanate	1.25	
8-44-7A	Dodecenyl-2-aminoethyl ether	1.8	10.5
	1,4-Bis(isocyanatomethyl) cyclohexane	0.7	
8-44-8A	"Delta" silane*	1.8	14.0
	Menthane diisocyanate	0.7	

*Delta-aminobutylmethyldiethoxysilane.

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TABLE 45

BURNING PROPERTIES OF JP-4 GELLED WITH VARIOUS SYSTEMS

Weight of Gelled Fuel: 100 Grams

Run No.	Polyisocyanate Name	Wt %	Amine Name	Wt %	Wt % Total Additives	Remarks
6-39-1	Hexamethylene diisocyanate	0.8	Formonyte 608 (Oleyl amine)	2.8	3.6	The burning time was 8 minutes. The gel was 2 inches in diameter at start. While burning, the surface of the gel melted and flowed over an area approximately 12 inches in diameter.
6-39-2	Hylene TM-65 (Toluene diisocyanate)	1.3	Alamine 4D (Lauryl amine)	2.7	4.0	The burning time was 9 minutes. The gel was 2 inches in diameter at start. While burning, the gel flowed over an area approximately 4 inches in diameter. The gelled fuel bubbled while burning and released the fuel. It did practically no flowing.
6-39-3	Hexamethylene diisocyanate	1.2	2-Ethylhexyl-3-aminopropyl ether	2.8	4.0	When placed on a transite board this tough viscoelastic gel slowly flowed over an area approximately 4 inches in diameter. The burning time was 3 minutes. Once ignited, the entire mass of gel melted and spread over an area of 4 to 5 times its initial diameter (approximately 15 to 18 inches).

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TABLE 44

RATES OF GELATION USING VARIOUS GELLING AGENTS AT A TOTAL ADDITIVE CONCENTRATION OF 2.5 WEIGHT PERCENT

Run No.	Additive System	Wt % Additive	Gelation Rate, Seconds
8-41-1A	Lauryl amine	1.7	2.8
	Hylene TM-65	0.8	
8-41-2A	Oleyl amine	1.9	5.0
	Hexamethylene diisocyanate	0.6	
8-41-3A	2-Ethylhexyl-3-aminopropyl ether	1.75	4.0
	Hexamethylene diisocyarate	0.75	
8-41-4A	Dodecenyl-2-aminoethyl ether	1.9	4.0
	Hexamethylene diisocyanate	0.6	
8-42-1A	4-Chlorobenzylamine	1.4	0.2
	m-Xylylene diisocyanate	1.1	
8-42-2A	Lauryl amine	1.6	0.2
	Hexamethylene diisocyanate	0.9	
8-42-3A	"Delta" silane*	1.6	2.5
	Hexamethylene diisocyanate	0.9	
8-42-4A	Coco amine	1.4	4.5
	Naphthyl isocyanate	1.1	
8-42-5A	β-Ethoxyethylamine	1.0	0.09
	Naphthyl isocyanate	1.5	

TABLE 45 (Cont'd)

Run No.	Polyisocyanate Name	Wt %	Amine Name	Wt %	Wt % Total Additives	Remarks
7-38-1	Hylene TM-65	1.5	2-Ethylhexyl-amine	2.5	4.0	This system formed a weak visco-elastic gel. Had no form integrity. When burned, the fuel flowed over an area approximately twice the original size. Burning time was 7 minutes.
7-38-2	2,4,6-Toluene triisocyanate	1.25	2-Ethylhexyl-amine	2.75	4.0	This system formed a firm dilatant gel. When the gel was burned, it did not flow. Burning time was 8.5 minutes
7-38-3	Hexamethylene diisocyanate	1.0	Dodecenyl-2-aminoethyl ether	3.0	4.0	This system formed a viscoelastic gel. Once ignited, the gel melted and flowed over an area several times larger than the original area covered by the gel. Burning time was 3 minutes.
7-38-4	Menthane diisocyanate	1.35	Lauryl amine	2.65	4.0	This system formed a gel having a grease-like consistency. The gel did not melt or flow while burning. Burn-ing time was 6 minutes.
7-43-1A	3-Chlorophenyl isocyanate	2.2	4-Chlorobenzyl amine	1.8		Immediately formed a dry particulate gel, readily broken. When burned, the gel did not flow. Burning time was 11 minutes.

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TABLE 45 (Cont'd)

Run No.	Polyisocyanate Name	Wt %	Amine Name	Wt %	Wt % Total Additives	Remarks
7-50-2A	3-Chlorophenyl isocyanate	0.85	4-Chlorobenzyl amine	1.15	2.0	Immediately formed a very dry particulate gel, readily broken into small pieces. When burning, it did not flow. Burning time was 11 minutes.
8-1-1A	3-Chlorophenyl isocyanate	0.4	4-Chlorobenzyl amine	0.6	1.0	Gel properties and burning time was the same as in runs numbered 7-43-1A and 7-50-2A.
8-16-1A	m-Xylylene diisocyanate	1.6	p-Phenetidine	2.4	4.0	Required about 5 minutes to form a dry particulate gel. On burning, the gel did not flow. Burning time was 13 minutes.

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TABLE 46

BURNING PROPERTIES OF VARIOUS GELLED FUELS AT A TOTAL ADDITIVE CONCENTRATION OF 4.0 WEIGHT PERCENT

Quantity of Fuel Gel: 100 gms

Shape of Fuel Gel: 2-in. x 2.5-in. cylinder

Run No.	Additive System	Wt % Additives	Burning Properties	
			Burning Time, Min.	Area Increase While Burning*
8-45-1	2-Ethylhexyl-3-aminopropyl ether 4,6-Dimethyl-1,3-xylylene diisocyanate	2.3 1.7	5.0	3-4X
8-45-2	4-Isopropylbenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.3 1.7	16.0	0
8-45-3	β-Ethoxyethylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.9 2.1	16.0	0
8-45-4	n-Hexylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.3 1.7	15.0	0
8-45-5	Lauryl amine Hylene TM-65	2.7 1.3	8.0	1.5X
8-45-6	Oleyl amine Hexamethylene diisocyanate	3.02 0.98	8.0	6X
8-45-7	2-Ethylhexyl-3-aminopropyl ether Hexamethylene diisocyanate	2.8 1.2	4.0	10X
8-45-8	Dodecenyl-2-aminoethyl ether Hexamethylene diisocyanate	3.1 0.9	4.0	10X

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TABLE 46 (Cont'd)

Run No.	Additive System	Wt % Additives	Burning Properties	
			Burning Time, Min.	Area Increase While Burning*
8-45-9	4-Chlorobenzylamine m-Xylylene diisocyanate	2.3 1.7	16.5	0
8-45-10	Lauryl amine Hexamethylene diisocyanate	2.5 1.5	10.0	1.5X
8-46-1	"Delta" silane Hexamethylene diisocyanate	2.4 1.6	4.0	10X
8-46-2	Coco amine Naphthyl isocyanate	2.3 1.7	6.5	4X
8-46-3	Lauryl amine 4 6-Dimethyl-1,3-xylylene diisocyanate	2.5 1.5	16.5	0
8-46-4	β-Ethoxyethylamine Naphthyl isocyanate	1.5 2.5	5.5	4X
8-46-5	4-Chlorobenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.2 1.8	17.0	0
8-46-7	Oleyl amine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.8 1.2	5.5	3X

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TABLE 46 (Cont'd)

Run No.	Additive System	Wt % Additives	Burning Properties	
			Burning Time, Min.	Area Increase While Burning*
8-46-8	Dodecenyl-2-aminoethyl ether	2.9	5.0	4X
	1,4-Bis(isocyanato methyl) cyclohexane	1.1		
8-46-9	"Delta" silane	3.0	7.5	1.5X
	Menthane diisocyanate	1.0		

*This column lists the increase in area due to melting of the gel. For example, 4X means that the gel melted while burning and flowed over an area 4 times the initial area.

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TABLE 47

BURNING PROPERTIES OF VARIOUS GELLED FUELS AT A TOTAL ADDITIVE CONCENTRATION OF 2.5 WEIGHT PERCENT

Quantity of Fuel Gel: 100 gms
Shape of Fuel Gel: 2-in. x 2.5-in. cylinder

Run No.	Additive System	Wt % Additives	Burning Properties Burning Time, Min.	Burning Properties Area Increase While Burning*
8-45-2A	4-Isopropylbenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.25 1.25	13.0	0
8-45-3A	β-Ethoxyethylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.25 1.25	14.0	0
8-45-4A	n-Hexylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.2 1.3	13.0	0
8-45-5A	Lauryl amine Hylene TM-65	1.7 0.8	5.5	2.5X
8-45-6A	Oleyl amine Hexamethylene diisocyanate	1.9 0.6	5.0	6X
8-45-7A	2-Ethylhexyl-3-aminopropyl ether Hexamethylene diisocyanate	1.75 0.75	3.5	10X
8-45-8A	Dodecenyl-2-aminoethyl ether Hexamethylene diisocyanate	1.9 0.6	4.0	10X

TABLE 47 (Cont'd)

Run No.	Additive System	Wt % Additive	Burning Properties Burning Time, Min.	Burning Properties Area Increase While Burning*
8-45-9A	4-Chlorobenzylamine m-Xylylene diisocyanate	1.4 1.1	13.5	0
8-45-10A	Lauryl amine Hexamethylene diisocyanate	1.6 0.9	8.0	2X
8-46-1A	"Delta" silane Hexamethylene diisocyanate	1.6 0.9	4.0	10X
8-46-2A	Coco amine Naphthyl isocyanate	1.4 1.1	5.5	6X
8-46-3A	Lauryl amine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.6 0.9	15.5	0
8-46-4A	β-Ethoxyethylamine Naphthyl isocyanate	1.0 1.5	4.0	5X
8-46-5A	4-Chlorobenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.35 1.15	13.0	0
8-46-7A	Oleyl amine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.75 0.75	4.5	4X

TABLE 47 (Cont'd)

Run No.	Additive System	Wt % Additive	Burning Properties	
			Burning Time, Min.	Area Increase While Burning*
8-46-8A	Dodecenyl-2-aminoethyl ether	1.8	4.5	6X
	1,4-Bis(isocyanatomethyl) cyclohexane	0.7		
8-46-9A	"Delta" silane	1.8	6.0	2X
	Menthane diisocyanate	0.7		

*This column lists the increase in area due to melting of the gel. For example, 4X means that the gel melted while burning and flowed over an area 4 times the initial area.

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TABLE 48

EVALUATION OF VARIOUS GELS UNDER IMPACT CONDITIONS

Container Opening: 1.5" × 0.5"
Fuel Gelled: 300 Grams

Run No.	Additives	Wt % Additive	Wt % Total Additives	Gel Type	Impact Force in G's	Remarks
6-21-1	Lauryl amine Hylene TM-65	2.7 1.3	4.0	Particulate	268	On impact, 11.0 grams of gel were knocked out. The pieces flew forward about 6 to 8 feet and "splattered" on hitting the ground.
6-22-2	Oleyl amine Hexamethylene diisocyanate	2.7 1.3	4.0	Particulate	268	On impact, 9.0 grams of gel were thrown 4 to 5 feet from the hole in the container.
6-45-1	Oleyl amine Hexamethylene diisocyanate	2.7 1.3	4.0	Particulate	268	In repeating the above run, 8 grams of gel emerged from the opening. On emerging from the hole, it appeared to break into several pieces.
6-45-2	Amine 803 Hexamethylene diisocyanate	2.8 1.2	4.0	Viscoelastic	580	On the first impact, the gel remained in the container. On the second impact, a small quantity of the gel emerged from the hole and hung over the edge of the hole. None of the gel was thrown free of the container.

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TABLE 49

EVALUATION OF VARIOUS GELS UNDER IMPACT CONDITIONS

Impact Force: 580 G's
Container Opening: 2-5/8" x 5/8"
Fuel Gelled: 300 gms

Run No.	Additives	Wt % Additive	Wt % Total Additives	Gel Type	Remarks
8 14-1	4-Chlorobenzylamine m-Xylylene diisocyanate	2.3 1.7	4.0	Dry particulate	On impact, 23 grams of gel were knocked out. The gel ignited when thrown through a flame and continued burning after hitting the ground.
8-14-2	"Delta" silane* Menthane diisocyanate	2.9 1.0	3.9	Elastomeric	14 grams of gel were knocked out on impact. The gel did not ignite when thrown through the fire.
8 21-1	Lauryl amine Hylene TM-65	2.7 1.3	4.0	Particulate	17 grams were lost on impact. The gel ignited when thrown through the flame.
8 21-2	Oleyl amine Hexamethylene diisocyanate	3.02 0.98	4.0	Particulate	Gel lost 17 grams on impact. Gel ignited when thrown through flame.
8 21-3	t-Octyl amine Hylene TM-65	2.45 1.55	4.0	Dry particulate	Lost 14 grams of gel on impact. Gel did not ignite when thrown through flame.
8 22-1	Amine 803 Hexamethylene diisocyanate	2 76 1.24	4 0	Viscoelastic	No gel was thrown from the container.

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TABLE 49 (Cont'd)

Run No.	Additives	Wt % Additive	Wt % Total Additives	Gel Type	Remarks
8-22-2	Lauryl amine Hexamethylene diisocyanate	2.45 1.55	4.0	Particulate	System lost 21 grams on impact Gel ignited when thrown through flame.
8-22-3	"Delta" silane Hexamethylene diisocyanate	2.4 1 o	4 0	Viscoelastic	Lost 21 grams on impact. Gel ignited when thrown through flame.
8-22-5	4-Chlorobenzyl amine 3-Chlorophenyl isocyanate	1.8 2.2	4.0	Dry particulate	Lost 27 grams on impact. Gel ignited when thrown through flame

*Delta - Aminobutylmethyldiethoxysilane

TABLE 50

IMPACT PROPERTIES OF VARIOUS GELS AT A TOTAL ADDITIVE CONCENTRATION OF 4.0 WEIGHT PERCENT

Impact Force: 580 G's
Container Opening: 2-5/8" x 5/8"
Fuel Gelled: 300 gms

Run No.	Additive System	Wt % Additive	Gel Type	Wt % of Gel Lost
9-6-4	4-Isopropylbenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.3 1.7	Dry Particulate	Not run
9-6-5	β-Ethoxyethylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.9 2.1	Dry Particulate	6
9-6-6	n-Hexylamine 4 6-Dimethyl-1,3-xylylene diisocyanate	2.3 1.7	Particulate	6
9-7-1	Lauryl amine Hylene TM-65	2.7 1.3	Particulate	5
9-7-2	Oleyl amine Hexamethylene diisocyanate	3.02 0.98	Particulate	5
9-7-3	2-Ethylhexyl-3-aminopropyl ether Hexamethylene diisocyanate	2.8 1.2	Viscoelastic	0
9-7-4	Dodecenyl-2-aminoethyl ether Hexamethylene diisocyanate	3.1 0.9	Viscoelastic	0
9-7-5	4-Chlorobenzylamine m-Xylylene diisocyanate	2.3 1.7	Dry Particulate	7

TABLE 50 (Cont'd)

Run No.	Additive System	Wt % Additive	Gel Type	Wt % of Gel Lost
9-7-6	Lauryl amine Hexamethylene diisocyanate	2.5 1.5	Dry Particulate	6
9-8-1	"Delta" silane Hexamethylene diisocyanate	2.4 1.6	Viscoelastic	6
9-8-2	Coco amine Naphthyl isocyanate	2.3 1.7	Particulate	4
9-8-3	Lauryl amine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.5 1.5	Dry Particulate	5
9-8-4	β-Ethoxyethylamine Naphthyl isocyanate	1.5 2.5	Dry Particulate	6
9-8-5	4-Chlorobenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.2 1.8	Dry Particulate	6
9-8-6	Oleyl amine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.8 1.2	Weak Thixotropic	Too weak
9-9-1	Dodecenyl-2-aminoethyl ether 1,4-Bis(isocyanatomethyl) cyclohexane	2.9 1.1	Viscoelastic - Particulate	5
9-9-2	"Delta" silane Menthane diisocyanate	3.0 1.0	Viscoelastic - Particulate	4

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TABLE 51

IMPACT PROPERTIES OF VARIOUS GELS AT A TOTAL ADDITIVE CONCENTRATION OF 2.5 WEIGHT PERCENT

Impact Force: 580 G's
Container Opening: 2-5/8" x 5/8"
Fuel Gelled: 300 gms

Run No.	Additive System	Wt % Additive	Gel Type	Wt % of Gel Lost
9-4-1	4-Isopropylbenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.25 1.25	Dry Particulate	Not run
9-4-2	β-Ethoxyethylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.25 1.25	Dry Particulate	9
9-4-3	n-Hexylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.2 1.3	Particulate	6
9-4-4	Lauryl amine Hylene TM-65	1.7 0.8	Particulate	5
9-4-5	Oleyl amine Hexamethylene diisocyanate	1.9 0.6	Particulate	5
9-4-6	2-Ethylhexyl-3-aminopropyl ether Hexamethylene diisocyanate	1.75 .75	Viscoelastic	0
9-4-7	Dodecenyl-2-aminoethyl ether Hexamethylene diisocyanate	1.9 0.6	Viscoelastic	0
9-4-8	4-Chlorobenzylamine m-Xylylene diisocyanate	1.4 1.1	Dry Particulate	8
9-5-1	Lauryl amine Hexamethylene diisocyanate	1.6 0.9	Dry Particulate	7

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TABLE 51 (Cont'd)

Run No.	Additive System	Wt % Additive	Gel Type	Wt % of Gel Lost
9-5-2	"Delta" silane Hexamethylene diisocyanate	1.6 0.9	Viscoelastic	8
9-5-3	Coco amine Naphthyl isocyanate	1.4 1.1	Particulate	7
9-5-4	Lauryl amine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.6 0.9	Dry Particulate	6
9-5-5	β-Ethoxyethylamine Naphthyl isocyanate	1.0 1.5	Dry Particulate	8
9-5-6	4-Chlorobenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.35 1.15	Dry Particulate	6
9-6-1	Oleyl amine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.75 0.75	Weak Thixotropic	Too weak
9-6-2	Dodecenyl-2-aminoethyl ether 1,4-Bis(isocyanato	1.8 0.7	Viscoelastic-Particulate	6
9-6-3	"Delta" silane Menthane diisocyanate	1.8 0.7	Viscoelastic-Particulate	5

TABLE 52

DETERMINATION OF TEMPERATURE LIMITS FOR VARIOUS GELLING SYSTEMS

Run No.	Additive System	Wt % Additive	Wt % Total Additives	JP-4 Temp. °C	Remarks
6-2-1A	Hexamethylene diisocyanate Oleyl amine	1.2 2.8	4.0	40	Above this temperature, gel loses strength.
6-2-5	Hexamethylene diisocyanate Oleyl amine	1.2 2.8	4.0	-10	Rapidly gelled JP-4 gel is somewhat weaker than obtained above. This is considered the lower temperature limit.
6-3-3	Hexamethylene diisocyanate Alamine 4D (lauryl amine)	1.0 1.8	2.8	40	This is the maximum temperature at which a gel can be obtained.
6-3-3A	Hexamethylene diisocyanate Alamine 4D (lauryl amine)	1.0 1.8	2.8	0	Does not form a gel because amine is not soluble in JP-4 at 0°C.
6-30-3	Hexamethylene diisocyanate 2-Ethylhexyl-3-amino propyl ether	1.2 2.8	4.0	60	The JP-4 and amine were warmed to 60°C. The diisocyanate was then added. At this temperature range this system required approximately 20 to 30 seconds to completely gel the fuel.
7-2-1	Hexamethylene diisocyanate 2-Ethylhexyl-3-amino-propyl ether	1.2 2.8	4.0	-58	Addition of the diisocyanate rapidly converted the fuel to a dry, very hard gel. On warming, the gel became viscoelastic.

TABLE 52 (Cont'd)

Run No.	Additive System	Wt % Additive	Wt % Total Additives	JP-4 Temp. °C	Remarks
8-34-1	"Delta" silane* 4,6-Dimethyl-1,3-xylylene diisocyanate	2.6 1.4	4.0	65	Instantly formed a good gel.
8-34-2	"Delta" silane* 4,6-Dimethyl-1,3-xylylene diisocyanate	2.6 1.4	4.0	-40	Instantly gelled the fuel. Considered to be lowest temperature because gel loses some of its cohesive strength.
8-34-3	Oleyl amine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.9 1.1	4.0	65	Rapidly formed a good gel.
8-34-3A	Oleyl amine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.9 1.1	4.0	-27	Instantly formed a good dry gel. Gel starting to lose some of its strength.
8-34-4	β-Ethoxyethylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.6 2.4	4.0	65	Rapidly gelled the fuel. The rate was too fast to obtain good mixing.
8-34-4A	β-Ethoxyethylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.6 2.4	4.0	-40	Instantaneously formed a particulate gel.

*Delta: Aminobutylmethyldiethoxysilane

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TABLE 53

DETERMINATION OF TEMPERATURE LIMITS FOR VARIOUS GELLING SYSTEMS
USING 4.0 WEIGHT PERCENT ADDITIVES

Run No.	Additive System	Wt % Additive	Temperature Limits		Remarks
			Lower °C	Upper °C	
8-50-3	4-Isopropylbenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.3 1.7	-10	60	Good gel at both temperatures.
8-50-4	β-Ethoxyethylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.9 2.1	-30	60	Formed a fair gel at the lower temperature.
8-50-4	n-Hexylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.3 1.7	-40	60	Formed a fair gel at both temperature limits.
9-1-1	Lauryl amine Hylene TM-65	2.7 1.3	0	38	Poor gels were formed at both temperature limits.
9-1-2	Oleyl amine Hexamethylene diisocyanate	3.02 0.98	-10	40	A weak gel was formed at -10°C.
9-1-3	2-Ethylhexyl-3-aminopropyl ether Hexamethylene diisocyanate	2.8 1.2	-55	60	Good gel at both temperatures.
9-1-4	Dodecenyl-2-aminoethyl ether Hexamethylene diisocyanate	3.1 0.9	-40	60	Good gel at both temperatures.
9-1-5	4-Chlorobenzylamine m-Xylylene diisocyanate	2.3 1.7	-40	60	Good gel at both temperatures.

TABLE 53 (Cont'd)

Run No.	Additive System	Wt % Additive	Temperature Limits		Remarks
			Lower °C	Upper °C	
9-2-!	Lauryl amine Hexamethylene diisocyanate	2.5 1.5	0	40	These temperature limits are the maximum.
8-50-1	"Delta" silane Hexamethylene diisocyanate	2.4 1.6	-40	60	At upper limit the rate of gelation was too slow.
9-2-3	Coco amine Naphthyl isocyanate	2.3 1.7	-10	60	Rate of gelation too slow at both temperatures.
9-2-4	Lauryl amine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.5 1.5	0	60	Fair gel obtained at 60°C.
9-2-5	β-Ethoxyethylamine Naphthyl isocyanate	1.5 2.5	-40	60	Fair gel obtained at both temperatures.
9-3-1	4-Chlorobenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.2 1.8	-40	60	Good gel obtained at both temperatures.
9-3-2	Oleyl amine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.8 1.2	-10	60	Fair gel obtained.
9-3-3	Dodecenyl-2-aminoethyl ether 1,4-Bis(isocyanatomethyl) cyclohexane	2.9 1.1	-40	60	Rate of gelation too slow at both temperatures.
9-3-4	"Delta" silane Menthane diisocyanate	3.0 1.0	0	50	Rate of gelation too slow at both temperatures.

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TABLE 54

PENETROMETER TESTS ON VARIOUS FUEL GELS

Run No.	Additive System	Wt % Additive	Wt % Total Additives	Hardness gm/in.²	Remarks
7-2-1	Hexamethylene diisocyanate Amine 803	1.4 2.6	4.0	900	At -58°C, gel is rigid and appears to be particulate. At 0°C and above, gel is viscoelastic.
6-4-1	Hylene TM-65 Lauryl amine	1.3 2.7	4.0	200	At low temperatures this system will not work due to the insolubility of the amine in JP-4.
6-41-1	Hylene TM-65 Octadecyl amine	1.05 2.95	4.0	275	Same as above.
6-4-2	Hexamethylene diisocyanate Oleyl amine	0.98 3.02	4.0	500	This system produces a particulate gel.
6-48-2	Hylene TM-65 t-Octyl amine	1.7 2.6	4.3	570	This system forms a good particulate gel; however, the rate of gelation is slow.
6-49-1	Hexamethylene diisocyanate Lauryl amine	1.55 2.45	4.0	450	This system forms a firm particulate gel.

TABLE 54 (Cont'd)

Run No.	Additive System	Wt % Additive	Wt % Total Additives	Hardness gm/in.^{2}	Remarks
8-28-1A	4-Chlorobenzylamine 4, 6-Dimethyl-1, 3-xylyline diisocyanate	2.5 2.0	4.5	600	This system formed a dry particulate gel with very little cohesive strength.
8-29-1A	Amine 803 4, 6-Dimethyl-1, 3-xylylene diisocyanate	2.4 1.8	4.2	127	This system formed a weak particulate gel with good cohesive strength.
6-29-3A	Lauryl amine 4, 6-Dimethyl-1, 3-xylylene diisocyanate	2.5 1.5	4.0	600	Instantaneously formed a good particulate gel.
8-29-4A	p-Phenetidine 4, 6-Dimethyl-1, 3-xylylene diisocyanate	2.4 2.0	4.4	318	Formed a weak, dry, particulate gel.
8-30-3A	4-Isopropylbenzylamine 4, 6-Dimethyl-1, 3-xylylene diisocyanate	3.0 2.2	5.2	225	Rapidly formed a dry particulate gel.
8-30-4A	β-Ethoxyethylamine 4, 6-Dimethyl-1, 3-xylylene diisocyanate	2.0 2.0	4.0	485	Instantaneously formed a dry particulate gel.
8-31-3A	n-Hexylamine 4, 6-Dimethyl-1, 3-xylylene diisocyanate	2.0 2.2	4.2	230	Instantaneously formed a particulate gel.

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TABLE 54 (Cont'd)

Run No.	Additive System	Wt % Additive	Wt % Total Additives	Hardness gm/in.^{2}	Remarks
7-43-1B	3-Chlorophenyl isocyanate 4-Chlorobenzylamine	2.2 1.8	4.0	125	This system forms a firm particulate gel. It is readily broken.
7-50-2B	m-Xylylene diisocyanate 4-Chlorobenzylamine	0.85 1.15	2.0	410	This system forms a very dry particulate gel. It readily crumbles.
8-6-1B	m-Xylylene diisocyanate 4-Chlorobenzylamine	1.6 2.4	4.0	395	Instantaneously forms a firm, dry, particulate gel. It readily crumbles.
8-7-1B	m-Xylylene diisocyanate p-Phenetidine	1.6 2.4	4.0	550	Requires about 5 minutes to form a hard, dry, particulate gel. It readily crumbles.
9-21-1	Coco amine Naphthyl isocyanate	2.3 1.7	4.0	400	This system forms a firm particulate gel having little cohesive strength.
9-21-2	Dodecenyl-2-aminoethyl ether 1,4-Bis(isocyanatomethyl) cyclohexane	2.9 1.1	4.0	380	This gel is between a viscoelastic and particulate type of gel.
9-21-3	"Delta" silane Menthane diisocyanate	3.0 1.0	4.0	210	Gel is between a viscoelastic and particulate type of gel.

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TABLE 55

SPARK IGNITION TESTS ON GELS CONTAINING 4.0 WEIGHT PERCENT ADDITIVES

Run No.	Additive System	Wt % Additive	Air Velocity liters/min*
9-11-1	JP-4 only	0.0	20.0
9-12-4	4-Isopropylbenzylamine 4, 6-Dimethyl-1, 3-xylylene diisocyanate	2.3 1.7	6.0
9-13-6	β-Ethoxyethylamine 4, 6-Dimethyl-1, 3-xylylene diisocyanate	1.9 2.1	5.5
9-12-5	n-Hexylamine 4, 6-Dimethyl-1 3-xylylene diisocyanate	2.3 1.7	4.5
9-13-5	Lauryl amine Hylene TM-65	2.7 1.3	3.0
9-12-1	Oleyl amine Hexamethylene diisocyanate	3.02 0.98	6.0
9-11-4	2-Ethylhexyl-3-aminopropyl ether Hexamethylene diisocyanate	2.8 1.2	4.5
9-11-2	Dodecenyl-2-aminoethyl ether Hexamethylene diisocyanate	3.1 0.9	4.5

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TABLE 55 (Cont'd)

Run No.	Additive System	Wt % Additive	Air Velocity, liters/min*
9-13-1	4-Chlorobenzylamine m-Xylylene diisocyanate	2.3 1.7	4.5
9-12-2	Lauryl amine Hexamethylene diisocyanate	2.5 1.5	5.0
9-12-3	"Delta" silane Hexamethylene diisocyanate	2.4 1.6	6.0
9-12-6	Coco amine Naphthyl isocyanate	2.3 1.7	5.5
9-12-7	Lauryl amine 4, 6-Dimethyl-1, 3-xylylene diisocyanate	2.5 1.5	4.0
9-12-8	β-Ethoxyethylamine Naphthyl isocyanate	1.5 2.5	10.0
9-11-3	4-Chlorobenzylamine 4, 6-Dimethyl-1, 3-xylylene diisocyanate	2.2 1.8	2.5
9-13-2	Oleyl amine 4, 6-Dimethyl-1, 3-xylylene diisocyanate	2.8 1.2	8.0
9-13-3	Dodecenyl-2-aminoethyl ether 1, 4-Bis(isocyanatomethyl) cyclohexane	2.9 1.1	3.5
9-13-4	"Delta" silane Menthane diisocyanate	3.0 1.0	2.5

*The maximum air velocity in which the vapors can be ignited with a Tesla coil.

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TABLE 56

SPARK IGNITION TESTS ON GELS CONTAINING 2.5 WEIGHT PERCENT ADDITIVES

Run No.	Additive System	Wt % Additive	Air Velocity, liters/min*
9-14-4	4-Isopropylbenzylamine	1.25	7.5
	4,6-Dimethyl-1,3-xylylene diisocyanate	1.25	
9-15-2	β-Ethoxyethylamine	1.25	10.2
	4,6-Dimethyl-1,3-xylylene diisocyanate	1.25	
9-13-9	n-Hexylamine	1.2	10.2
	4,6-Dimethyl-1,3-xylylene diisocyanate	1.3	
9-14-1	Lauryl amine	1.7	5.0
	Hylene TM-65	0.8	
9-14-2	Oleyl amine	1.9	6.5
	Hexamethylene diisocyanate	0.6	
9-14-6	2-Ethylhexyl-3-aminopropyl ether	1.75	5.0
	Hexamethylene diisocyanate	0.75	
9-14-5	Dodecenyl-2-aminoethyl ether	1.9	5.0
	Hexamethylene diisocyanate	0.6	
9-13-8	4-Chlorobenzylamine	1.4	9.0
	m-Xylylene diisocyanate	1.1	

TABLE 56 (Cont'd)

Run No.	Additive System	Wt % Additive	Air Velocity liters/min*
9-15-7	Lauryl amine	1.6	5.5
	Hexamethylene dii ocyanate	0.9	
9-14-3	"Delta" silane	1.6	6.0
	Hexamethylene diisocyanate	0.9	
9-15-1	Coco amine	1.4	5.5
	Naphthyl isocyanate	1.1	
9-14-7	Lauryl amine	1.6	9.0
	4, 6-Dimethyl-1, 3-xylylene diisocyanate	0.9	
9-15-3	β-Ethoxyethylamine	1.0	11.5
	Naphthyl isocyanate	1.5	
9-13-7	4-Chlorobenzylamine	1.35	9.0
	4, 6-Dimethyl-1, 3-xylylene diisocyanate	1.15	
9-15-6	Oleyl amine	1.75	8.5
	4, 6-Dimethyl-1, 3-xylylene diisocyanate	0.75	
9-15-5	Dodecenyl-2-aminoethyl ether	1.8	4.5
	1, 4-Bis(isocyanatomethyl) cyclohexane	0.7	
9-15-4	"Delta" silane	1.8	6.0
	Menthane diisocyanate	0.7	

*The maximum air velocity in which the vapors can be ignited with a Tesla coil.

TABLE 57

CODE USED FOR COMPARING THE VARIOUS GELS

Evaluation Tests	Ratings									
	10	9	8	7	6	5	4	3	2	1
1. Penetrometer Test, gm/in.²	600 - 550	550 - 500	500 - 450	450 - 400	400 - 350	350 - 300	300 - 250	250 - 200	200 - 150	150 - 0
2. Rate of Gelation, seconds	0.0 - 0.05	0.05 - 0.1	0.1 - 0.3	0.3 - 0.6	0.6 - 1.0	1.0 - 2.0	2.0 - 3.0	3.0 - 4.0	4.0 - 5.0	>5.0
3. Impact Properties, wt % gel lost	0 - 1	0 - 2	2 - 3	3 - 4	4 - 5	5 - 6	6 - 7	7 - 8	8 - 9	9 - 10
4. Temperature Limits, °C; ratings also include influence of temperature on gelation rate and gel properties	(-40° to 60°)		(-30° to 60°)		(-20° to 60°)		(-10° to 60°)		(0° to 60°)	
5. Burning Properties:										
a. Time in minutes	15 - 13	13 - 10	10 - 8	8 - 7	7 - 6	6 - 5	5 - 4	4 - 3	3 - 2	2 - 1
b. Area increase while burning	0 - 1	1 - 2	2 - 3	3 - 4	4 - 5	5 - 6	6 - 7	7 - 8	8 - 9	9 - 10
6. Spark Ignition Properties: Air velocity required to decrease fuel vapors below explosive limits, liters/min.	2 - 3	3 - 4	4 - 5	5 - 6	6 - 7	7 - 8	8 - 9	9 - 10	10 - 11	11 - 12

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TABLE 58

COMPARISON OF VARIOUS GELS USING A TOTAL ADDITIVE
CONCENTRATION OF 4.0 WEIGHT PERCENT

Additive System	Wt % Additive	Gel Type	Gelling Rate	Gel Rigidity	Impact Rating	Temperature Range	Burning Rate	Flow While Burning	Spark Ignition	Total
Lauryl amine (Armeen 12) Hylene TM-65	2.7 1.3	Particulate	5	3	6	1	8	9	10	42
4-Isopropylbenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.3 1.7	Dry Particulate	9	3	2	4	10	10	7	45
β-Ethoxyethylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.0 2.0	Dry Particulate	9	8	5	7	10	10	7	56
Hexylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.9 2.1	Particulate	10	3	5	9	10	10	8	55
Oleyl amine Hexamethylene diisocyanate	3.02 0.98	Particulate	3	9	6	3	8	5	7	41
2-Ethylhexyl-3-aminopropyl ether Hexamethylene diisocyanate	2.8 1.2	Viscoelastic	4	1	10	10	3	1	8	37
Dodecenyl-2-aminoethyl ether Hexamethylene diisocyanate	3.1 0.9	Viscoelastic	3	1	10	10	3	1	8	36
4-Chlorobenzylamine m-Xylylene diisocyanate	2.3 1.7	Dry Particulate	8	9	4	10	10	10	8	59
Lauryl amine Hexamethylene diisocyanate	2.5 1.5	Dry Particulate	5	8	5	1	9	9	8	45
Delta - aminobutylmethyldiethoxysilane Hexamethylene diisocyanate	2.4 1.6	Viscoelastic	5	1	5	8	6	1	6	31
Coco amine (Formonyte 601) Naphthyl isocyanate	2.3 1.7	Particulate	4	7	7	3	6	6	7	40
Lauryl amine (Formonte 616) 4,6-Dimethyl-1,3-xylylene diisocyanate	2.5 1.5	Dry Particulate	9	10	6	1	10	10	9	55
β-Ethoxyethyl amine Naphthyl isocyanate	1.5 2.5	Dry Particulate	9	8	5	9	5	4	2	42
4-Chlorobenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	2.2 1.8	Dry Particulate	9	10	5	10	10	10	10	64
Oleyl amine (Formonyte 608) 4,6-Dimethyl-1,3-xylylene diisocyanate	2.8 1.2	Weak Thixotropic	8	1	1	3	5	8	5	31
Dodecenyl-2-aminoethyl ether 1,4-Bis(isocyanatomethyl) cyclohexane	2.9 1.1	Viscoelastic-Particulate	2	6	5	9	5	7	9	43
Delta - aminobutylmethyldiethoxysilane Menthane diisocyanate	3.0 1.0	Viscoelastic-Particulate	1	3	7	1	7	9	10	38

TABLE 59

COMPARISON OF VARIOUS GELS USING A TOTAL ADDITIVE
CONCENTRATION OF 2.5 WEIGHT PERCENT

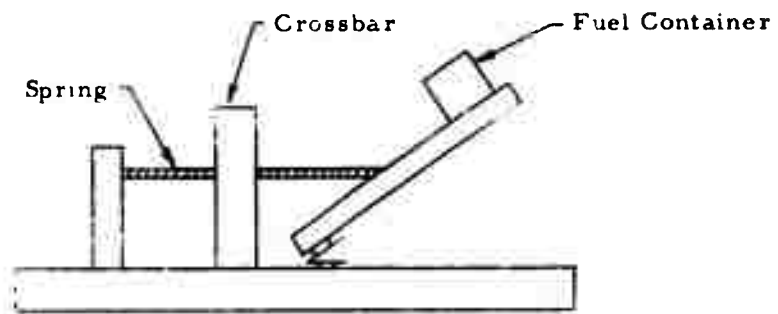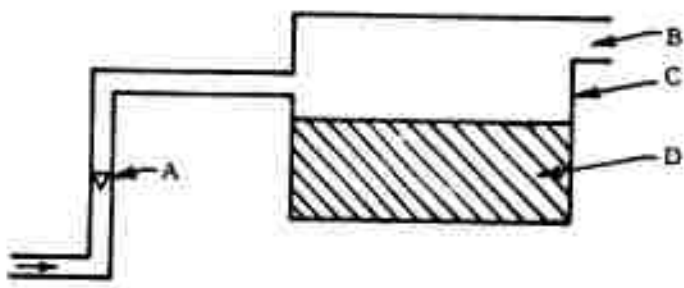| Additive System	Wt % Additive	Gel Type	Gelling Rate	Impact Rating	Burning Rate	Flow While Burning	Spark Ignition	Total
4-Isopropylbenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.25 1.25	Dry Particulate	3	-	9	10	5	-
β-Ethoxyethylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.25 1.25	Dry Particulate	9	1	10	10	2	32
n-Hexylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.2 1.3	Particulate	10	5	9	10	2	36
Lauryl amine Hylene TM-65	1.7 0.8	Particulate	8	5	5	8	8	34
Oleyl amine Hexamethylene diisocyanate	1.9 0.6	Particulate	8	5	4	5	6	28
2-Ethylhexyl-3-aminopropyl ether Hexamethylene diisocyanate	1.75 0.75	Viscoelastic	2	10	3	1	8	24
Dodecenyl-2-aminoethyl ether Hexamethylene diisocyanate	1.9 0.6	Viscoelastic	2	10	4	1	8	25
4-Chlorobenzylamine m-Xylylene diisocyanate	1.4 1.1	Dry Particulate	8	3	9	10	4	34
Lauryl amine Hexamethylene diisocyanate	1.6 0.9	Dry Particulate	8	4	8	8	7	35
"Delta" silane Hexamethylene diisocyanate	1.6 0.9	Viscoelastic	4	3	4	1	7	19
Coco amine Naphthyl isocyanate	1.4 1.1	Particulate	2	4	5	5	7	23
Lauryl amine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.6 0.9	Dry Particulate	9	5	10	10	4	38
β-Ethoxyethylamine Naphthyl isocyanate	1.0 1.5	Dry Particulate	9	2	4	6	1	22
4-Chlorobenzylamine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.35 1.15	Dry Particulate	9	6	9	10	4	38
Oleyl amine 4,6-Dimethyl-1,3-xylylene diisocyanate	1.75 0.75	Weak Thixotropic	8	-	4	4	4	-
Dodecenyl-2-aminoethyl ether 1,4-Bis(isocyanatomethyl) cyclohexane	1.8 0.7	Viscoelastic-Particulate	1	5	4	5	8	23
"Delta" silane Menthane diisocyanate	1.8 0.7	Viscoelastic-Particulate	1	6	6	9	7	29

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FIGURE 1. EQUIPMENT FOR DETERMINATION OF
IMPACT PROPERTIES OF GELLED JP-4

A. Flow Meter
B. Air-Vapor Exit. Cross-Sectional Area: 0.7 cm^2
C. Fuel Gel Container. Cross-Sectional Area: 10.0 cm^2
D. Fuel Gel. Surface Area: 31.0 cm^2

FIGURE 2. EQUIPMENT FOR DETERMINATION OF
SPARK IGNITION TESTS

APPENDIX III
LITERATURE SEARCH

1. Alm, R. M., U. S. Patent 2,668,098 (to Standard Oil), 1954.
    C. A. **48**, 5486$_c$ (1954).

    Gelling normally liquid hydrocarbons using 0.5 to 10
    weight percent of a metal salt of an aliphatic zanthate
    having a polymethyl alkyl group containing between
    12 to 25 carbon atoms.

-   Beerbower, Alan, Richards H. A., U. S. Patent 2,455,649
    (to Standard Oil Development Co.), 1948. C. A. **43**,1960$_c$ (1949).

    Obtained a solidified oil using a mixture consisting of 3.5
    parts stearic acid, 1.75 parts wood rosin, 3.0 parts castor
    oil, 3.0 parts kerosene, 85 parts gasoline, 2 parts
    50 percent aqueous sodium hydroxide, and 2 parts water.

3. Berezniak, A., "Sodium and Aluminum Salts of Rapeseed Oil
    Fatty Acids as Thickening Agents for Liquid Fuels", Biul.
    Wojskowej Arad. Tech. Volume 6, No. 32, pp 21-35, 1957.
    C. A. **53**,4711$_i$ (1959).

    The sodium and aluminum salts of fatty acids from rapeseed
    oils were used as thickening agents to prepare gasoline
    gels. The monohydroxy acids were found to be the most
    suitable in concentrations of less than 10 percent in
    gasoline.

4. Bertheir, R. F.

    French Patent 860,470 (1941)
    French Patent 860,471 (1941)
    French Patent 860,472 (1941)
    French Patent 860,473 (1941)

    Gasoline is mixed with alkali soluble tylose and caustic soda
    to give a gel. In French Patent 860,471, legumins are
    mixed with above. In French Patent 860,472, the water
    solution complexes with the additives in French Patents

860, 470-1. The mixture is made insoluble by adding a heavy metal salt such as $CuSO_4$. In French Patent 860, 473, Cn, Zn, or Al alginate with an excess of NH_3 forms gas gels. Evaporation of the NH_3 forms insoluble alginates.

5. Bertheir, R. F., Labour, J. F. P. E., French Patent 948, 267, (1949). C. A. **45**, 4032$_b$ (1951).

   Purified alginic acid by boiling with 3 percent barium hydroxide and sodium hydroxide for 6 hours. The free acid is then filtered and dried. Pure alginic acid thus formed will gel hydrocarbons.

6. Bertheir, R. F., Labour, J. F. P. E., French Patent 948, 268, (1949). C. A. **45**, 4032$_b$ (1951).

   Gelled hydrocarbons by mixing an alkali metal silicate with the hydrocarbon. The soluble silicate is converted to silicic acid which gels the hydrocarbons.

7. Bertheir, R. F., Labour, J. F. P. E., French Patent 948, 269, (1949). C. A. **45**, 4032$_b$ (1951).

   Silicate gels of gasoline may be stabilized by addition of a 1-percent solution of sodium borate or aluminum hydroxide.

8. Biswell, C. B., U. S. Patent 2, 873, 178 (to E. I. Du Pont de Nemours), 1959. C. A. **53**, 9652$_b$ (1959).

   Gasoline is gelled by incorporating 0.05-1 weight percent Cu^{++} followed by 0.05-1 weight percent mercaptan S. The copper is introduced as the naphthenate and the mercaptan S is derived from a primary aliphatic mercaptan.

9. Boulanger, C. L. J., French Patent 955, 472, (1950). C. A. **45**, 9257$_g$ (1951).

   Gasoline is dispersed in an aqueous colloidal solution such as methyl cellulose, gelatin, or casein, and the mix is gelled by adding a 10-percent solution of an ammonium salt such as ammonium borate.

10. Boulanger, C. L. J., French Patent 948,740 (1949). C. A. 45, 4032d (1951).

> Gasoline may be gelled by stirring in a closed rotating vessel with cellulose zanthate until a gel is formed which may be coagulated with an acid bath.

11. Bryant, W. C., Frost, H. Jr., U. S. Patent 2,594,286 (to Swan-Finch Oil Corp.), 1952. C. A. 46,7760g (1952).

> Prepared a hydrocarbon gelling agent by amidating polybasic acids with long chain primary amines. Required concentration ranges from 1 to 35 percent.

12. Buchanan, D. M., Menaul, P. L., U. S. Patent 2,860,103 (to Pan American Petroleum Corp.), 1958. C. A. 53, 5653i (1959).

> Hydrocarbons are temporarily gelled by adding 2 to 10 percent aluminum fatty acid soap, 0.5 to 3 percent water, and a nonionic emulsifier such as polyoxyethylene sorbitan monolaurate.

13. Carvley, C. M., Carlile, J. H. G., King, J. G., Kingman, F. E. T., "Aluminum Stearate Gels in Light Hydrocarbon Oils", J. Inst. Petroleum, Volume 33, pp 649-72, 1947.

> A study of peptizers for improving the stability of hydrocarbon gels together with a discussion of deleterious agents for such systems.

14. Cier, H. E., Schutze, H. G., U. S. Patent 2,794,003 (to Esso), 1957. C. A. 52, 1602d (1958).

> Hydrocarbons are gelled by the formation of Na, K, Ca, Ba, Hg, and Al derivatives of oil soluble sulfonyl chlorides of saturated paraffins of 6 to 16 carbon atoms in the hydrocarbon to be gelled.

15. Cohen, Leonard., U. S. Patent 2,718,462, (1955). C. A. 49, 16271i (1955).

Aluminum soaps of isooctoic acid (prepared from mixed heptenes by oxo process) are used to gel liquid hydrocarbons. Concentrations in the range of 1 to 4 percent form viscoelastic gels.

16. Continental Oil Company, British Patent 916,752, (1963). C. A. $\underline{58}$, 10033$_e$ (1963).

Gelling agents for gelling hydrocarbons for incendiary devices are prepared by treating a trialkylaluminum compound with SO_2 in the presence of hexane at -60°C. On warming to room temperature, a gel is obtained.

17. Copes, J. R., Mayhew, R. L., Williams, E. P., U. S. Patent 3,012,966 (to General Aniline Corp.), 1958. C. A. $\underline{56}$, 9017$_f$ (1962).

Hydrocarbons are thickened or gelled by mixing and heating or storing (1 - 12 days) 0.1 to 10 percent of a compound $[RC_6H_4O(CH_2)_3COO]_nM$ where R is a C_{6-10} alkyl group, M is H or an alkali metal or a basic ammonium group such as $(HOC_2H_4)_2NH_2$ and n is 1 or 2.

18. Donner, Jules, French Patent 633,731, (1927). C. A. $\underline{22}$, 3762 (1928).

A solution of soap in alcohol with lime water is added to hydrocarbon fuel to gel it. To restore to liquid, a small quantity of 10 percent $CaCl_2$ in water is added.

19. Dunn, F. R., Jr., Sauer, R. W., "Distillate Fuel Oil Gel", $\underline{Am.}$ $\underline{Soc. Testing Materials}$, Spec. Tech, Publ. No. 244, pp 47-56, 1958. C. A. $\underline{54}$, 20176$_c$ (1960).

Mercaptan content of fuel and exposure to brass cause fuel gelation in a degree proportional to the aromatic mercaptan concentration. Aliphatic mercaptans have a lower gel forming character.

20. Eigenberger, E., "Aluminum Salts of Higher Fatty Acids", $\underline{Fette \ U. \ Seifen,}$ Volume 49, pp 505-8, 1942.

The gelling properties of aluminum salts vary as the mono-,
di-, or tri-basic salts are formed and according to the prop-
erties of the acid. The salts of saturated fatty acids will
form gels at a lower concentration than will the correspond-
ing salts of unsaturated acids.

21. Eneberg, J. E. I., Swedish P .ent 174,147 (to Foersuarets
    Forskningsanstalt), 1961. C A. 56, 11733₁ (1962).

    The gelling agent consists of aluminum soaps of fatty
    aliphatic or cycloaliphatic acids plus an oxidation inhibitor,
    a chelating agent such as triethylene tetramine, and a pro-
    tective colloid such as carboxymethyl cellulose. A 5-percent
    solution of the gelling agent in commercial motor fuel at
    15 to 30°C after 0 to 10 minutes dispersion time yields a
    stable, elastic gel after 1 day of storage.

22. Farbenind, I. G., British Patent 339,360, (1929). C. A. 25,
    2497 (1931).

    To facilitate storage and handling, liquids such as benzene
    have formed in them a voluminous network of solid inorganic
    oxide or hydroxide such as might be produced by the action
    of a base on $SnCl_4$, $Fe Cl_3$, $AlCl_3$.

23. Farbenind, I. G., British Patent 339,660, (1929). C. A. 25,
    2734 (1931).

    Numerous details are listed on the recovery of hydrocarbon
    liquids from gelatinized materials.

24. Farbenind, I. G., British Patent 340,575, (1931). C. A. 25,
    2734 (1931).

    Liquid hydrocarbons are gelled by forming in them a
    voluminous framework by the action of ammonia or abietic
    acid or pimaric acid in the material to be gelled.

25. Faust, J., U. S. Patent 2,454,736 (to L. Sonneborn and Sons),
    1948. C. A. 43, 1959ₕ (1949).

Small quantities of phthalic acid esters convert mineral oil solutions to a rubbery gel.

26. Floyd, D. E., U. S. Patent 2,662,068 (to General Mills), 1953. C. A. <u>48</u>, 4222$_a$ (1954).

     The addition of polyamide gelling agents to hydrocarbons is described. These materials are used in incendiaries or flame throwers. The polyamide is obtained by reacting acetylmalonic ester and 1,3-diaminopropane.

27. Field, G. B., Markwood, W. H., U. S. Patent 3,020,133 (to Hercules Powder Co.), 1962. C. A. <u>56</u>, 11914$_f$ (1962).

     Describes the use of aluminum diisopropoxide mono-sec-butoxide as a gelling agent for hydrocarbons for incendiary purposes.

28. Fiero, G. W., "Hydrogenated Castor Oil as an Ointment Base", J. Am. Pharm. Assoc., Volume 29, pp 502-5, 1940. C. A. <u>35</u>, 851$_2$ (1941).

     Hydroxystearic acid is a jellifying material for liquid petroleum oils when used in quantities of 1 to 2 percent. Higher concentrations will form gels.

29. Finkelstein, L., U. S. Patent, 2,553,568 (to U. S. A.), 1951. C. A. <u>45</u>, 7354$_d$ (1951).

     Incendiary filling for bombs is prepared by mixing 3 parts stearic acid, 88.75 parts gasoline, 5 parts isobutyl methacrylate, and 2 parts calcium oxide. Careful addition of 1.25 parts water aids in control of thickening rate.

30. Fitzsimmons, V. G., Merker, R. L., Singleterry, C. R., "Phthalocyanines Lubricating Greases", Ind. Eng. Chem. Volume 44, pp 556-63, 1952.

     A nonsoap gelling agent for lubricating greases (phthalo-cyanine pigment) is described. Its advantages are greater resistance to thermal decomposition and oxidation at temperatures above 150°C.

31.   Fischer, K. A., Hecht, O. F., U. S. Patent 2,610,114,
       (to U. S. A.), 1952. C. A. 47, 3553h, (1953).

          Gasoline is emulsified by stirring with an equal volume
          of a 2-percent aqueous solution of sodium polyacrylate.
          The resultant emulsion is gelled by adding it dropwise to
          a 10-percent solution of calcium chloride.

32.   Gash, V. W., U. S. Patent 2,976,285 (to Monsanto), 1961.
       C. A. 55, 16574b (1961).

          A calcium chelate formed between calcium salts and 4-
          morpholine-4-(2-thienyl)-3-butene-2-one had the property
          to gel organic chemicals such as benzene, chloroform,
          and xylene.

33.   Gibson, P., Starmann, R. W., U. S. Patent 2,982,724 (to Swift
       and Co.), 1956. C. A. 56, 10463h (1962).

          Kerosene was gelled by adding 1 weight percent hydrogenated
          menhaden oil fatty acids containing a surfactant such as an
          alkyl aryl sulfonate. The acids were saponified using a
          25 percent aqueous solution of sodium hydroxide.

34.   Goff, W. H., Banks, W. L., U. S. Patent 2,789,040 (to Texas
       Co.), 1957. C. A. 51, 11616i (1957).

          Gelled gasoline may be formed by treating gasoline with an
          oxidized wax and sodium hydroxide. Preparation of the
          oxidized wax is described. Method of oxidized wax-sodium
          hydroxide-gasoline mixing is described.

35.   Gray, U. R., Alexander, A. E., "Composition Structure and
       Gelling Properties of Aluminum Soaps", J. Phys. and Colloid
       Chem., Volume 53, pp 23-9, 1949.

          Data lead to a polymeric formula for aluminum soaps with
          linked AlO octahedra joined by coordinate linkages and
          having acid chains extended sideways.

36. Gregory, J. N., "The Gelation of Gasoline as a Flame Thrower Fuel", J. Council Soc. Ind. Research, Volume 19, pp 153-6, 1946.

A mix of 5- to 7-percent 16-mesh "Geletral" and 1 percent Ethyl Cellosolve in gasoline gave a gel in 10-15 seconds. "Geletral" consists of 10 percent aluminum oxide and 2 percent 3-napthol as an antioxidant.

37. Griesinger, W. K., Canadian Patent 424, 914 (to Atlantic Refining Co.), 1945. C. A. $\underline{39}$, 1284_3 (1945).

A solid gel may be prepared by mixing a hydrocarbon distillate with 0.5 to 10 percent by volume of an aqueous solution containing petroleum sulfonates and 5 to 15 percent of a 10- to 40-percent aqueous alkali metal hydroxide.

38. Haden, W. L., Jr., Martin, C. O., U. S. Patent 2, 885, 360 (to Minerals and Chemicals Corp. of America), 1959. C. A. $\underline{53}$, 17492_c (1959).

Method is described for the gelation of gasoline, soybean oil, etc., using a dispersed natural clay.

39. Henning, O., "Gelation of Soaps in Hydrocarbons", Kolloid Z., Volume 169, pp 76-85, 1960.

Discusses the use of stearic acid, oleic acid, etc., to gel solutions of pure sodium stearate in hydrocarbons.

40. Herron, A. O., U. S. Patent 2, 684, 339 (to Safety Fuel and Chemical Corp.), 1954. C. A. $\underline{48}$, 11062_g (1954).

Discusses the preparation of a napalm composition consisting of the mixed aluminum salts of coconut fatty acids, naphthenic acid, and oleic acid.

41. Hotten, B. W., U. S. Patent 2, 709, 157 (to California Research Corp.), 1955. C. A. 49, 1286 (1955).

Symmetrical and unsymmetrical N, N'-diacylphenylene

diamines in which the acyl group contains 1 to 22 aliphatic carbon atoms which may be used as gelling agents.

42. Hotten, B. W., U. S. Patent 2,698,300 (to California Research Corp.), 1954. C. A. <u>49</u>, 4984$_f$ (1955).

Long chain monoacylureas may be used as gelling agents for lubricating greases.

43. Hotten, B. W., "Metal Terephthalamates - A New Class of Oil-Gelling Agents", <u>Ind. Eng. Chem.</u>, Volume 49, pp 1691-4, 1957.

The procedure for the preparation of substituted terephthalamates is given.

44. Hotten B. W., U. S. Patent 2,874,121 (to California Research Corp.), 1959. C. A. <u>53</u>, 9649$_f$ (1959).

Metal salts of monoalkyl terephthalates were used as gelling agents. Preparation procedure for monododecyl terephthalate is given. This material converted lubricating oils into a smooth gel.

45. Hunn, J. V., U. S. Patent 2,618,536 (to Sherwin-Williams Co.), 1952.

Combination of a liquid hydrocarbon and 0.5 to 20 percent of an alkoxy aluminum carboxylate having a general formula $[RO]_{n-1}$ Al $(XC=X)R']_{4-n}$, where R is an alkyl radical containing 1 to 3 carbon atoms and R' is an aliphatic radical containing 6 to 30 carbon atoms and X is O or S and n is 1 to 4 on the average, produces an anhydrous fuel gel.

46. Johnson, E. A., U. S. Patent 2,687,175 (to Standard Oil), 1954.

Hydrocarbon gels for fracturing oil-producing formations are prepared by adding 4 to 10 percent of a bodying agent (2-percent alkali metal soap plus 5-percent acetylene black) to gasoline or kerosene.

47. Losev, B. I., "Solids From Liquified Gases", Nousti, Neft. i Gaz. Tekhn, Gaz. Deld, No. 3, pp 30-4, 1961.

   Various methods are given for converting liquid fuels and liquified petroleum hydrocarbon gases into solid briquet. Storage, transportation, and uses of the bricks are discussed.

48. Mason, S., Goldstein, H. B., Cotter, J. F., U. S. Patent 2,758,123 (to Sun Chemical Corp.), 1956.

   Aluminum soaps of a mixture of several soap-forming acids are useful for gelation without heat of certain solvents.

49. McBain, J. W., Mysels, K. J., Smith, G. H., "Studies of Aluminum Soaps. VII. Aluminum Soaps in Hydrocarbons. The Gels and Jellies and Transformations Between Them". Trans. Faraday Soc., Volume 42B, pp 173-80, 1946.

   The aluminum soaps studied are di-and monolaurate, di-stearate, dioleate, dinaphthenate in benzene, isooctane, heptane, and cyclohexane.

50. McRoberts, T. S., Schulman, J. H., "Role of the Hydroxyl Group in the Gelation of Aluminum Soaps in Hydrocarbons". Nature, Volume 162, pp 101-2, 1948.

   Results of studies where water is added to in-situ produced solutions of aluminum soaps in hydrocarbon solvents (formed from aluminum alcoholates and fatty acids in solvent) are described.

51. McRoberts, T. S., Schulman, J. H., "Gelation of Aluminum Soaps in Gasoline", Proc. Roy. Soc. (London), Volume A200, pp 136-48, 1950.

   The results indicate the structure $R_1 - \overset{\text{OH}}{\underset{|}{Al}} - R_1$ is necessary for gelation where R is a fatty carboxyl group. The addition of water in a 1:1 ratio to aluminum is necessary to obtain maximum gelation.

52. Myerholtz, R. W., U. S. Patent 2,966,401 (to Standard Oil Co.), 1960. C. A. 55, 7830$_c$ (1961).

The interaction of alkali metals with a solution of a natural or synthetic rubber in any hydrocarbon will form a gel if heated to 46-48°C.

53. Mysels, K. J., U. S. Patent 2,492,173 (to U. S. A.), 1949. C. A. 44, 3247$_c$ (1950).

The flow of thickened fuels was investigated. It was concluded that the quantity of gasoline which can be pumped through a pipeline in time T can be increased by gelling to a thixotropic gel with metal soaps.

54. Mysels, K. J., "Napalm - Mixture of Aluminum Disoaps", Ind. and Eng. Chem., Volume 41, pp 1435-8, 1949.

Napalm is an aluminum soap derived from a mixed sodium soap of coconut and naphthenic and oleic acids. It is mainly a disoap with an average composition of 0.8 percent water, 1.7 percent inorganic material, and 7 percent uncombined materials of which 3 percent are unsaponificable and 70 percent free fatty acids.

55. Oscar Nevenschwander and Co., Swiss Patent 267,080, (1950). C.A. 45, 2193$_i$ (1951).

Aluminum salts of 2-ethylcaproic acid form gels with gasoline or solvent naphtha in concentrations of 3 to 6 weight percent.

56. Packter, A., "Slow Coagulation and Structure Formation in Concentrated Sols. I. Factors that Determine the Stability, Surface Potential, and Rates of Gelation of Thixotropic Insoluble-Metal-Salt Sols". Z. Physik Chem., Volume 211, pp 40-51, 1959. C. A. 53, 1463$_d$ (1959).

Stability of thixotropic sols of insoluble metal salts with anisometric particles was studied experimentally.

57. Poswick, J., Belgian Patent 576, 110 (to Ateliers de Constructions Electriques de Charleroi S.A.), 1959. C. A. <u>54</u>, 6154$_i$ (1960).

Gelation occurs when stoichiometric amounts of epoxy resin (molecular weight 1400 and epoxy equivalent 980) with 40-percent triisocyanate solution (reaction product from toluene diisocyanate, 3 moles; hexane triol, 1 mole; phenol, 3 moles) in a 1:1 ethylene glycol acetate-diethylene glycol diethyl ether mixture are combined.

58. Ratzer, A. F., Levin, D., U. S. Patent 2, 870, 095 (to Baker Industries, Inc.), 1959. C. A. <u>53</u>, 8618$_f$ (1959).

Liquid gelling agents for liquid hydrocarbons are prepared by use of a finely divided metal salt of a fatty acid suspended in a monomethyl ether of ethylene glycol.

59. Ring, K. A., U. S. Patent 2, 825, 409 (to Shell Development Co.), 1958. C. A. <u>52</u>, 11399$_f$ (1958).

Gels are formed using an alkali metal soap of tall oil acids.

60. Rinse, J., British Patent 772, 144 (to Hardman and Holden, Ltd.), 1957. C. A. <u>51</u>, 12549$_f$ (1957).

A condensation product having the properties of a gelling agent is obtained by heating an aluminum alcoholate of a monohydroxy alcohol.

61. Rinse, J., British Patent 809, 309 (to Hardman and Holden, Ltd.), 1959. C. A. <u>53</u>, 18863$_f$ (1959).

Preparation of aluminum-containing polymers is described which are useful as gelling agents, thickening agents, and waterproofing agents.

62. Shulman, G., U. S. Patent 2, 763, 621 (to Phillips Petroleum Co.), 1956. C. A. 51, 6996$_d$ (1957).

Preparation of hydroxy aluminum soaps capable of gelling liquid, light hydrocarbons is described.

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63.   Smith, G., Rogers, L. B., Mysels, K. J., "The Study of
       Aluminum Soap - Hydrocarbon Systems: Effect of Additives and
       Metathesis". J. Am. Oil Chemists' Soc., Volume 26, pp 135-
       38, 1949. C. A. $\underline{43}$, 3633$_i$ (1949).

       A study was made on the effect of additives on the rate of
       gelation.

64.   Stanley, D., Belgian Patent 622,731, (1963). C. A. $\underline{58}$, 13177$_b$
       (1963).

       Gelation of large volumes of aliphatic, aromatic, or halo-
       genated hydrocarbons, aromatic alcohols, or ethers was
       achieved by using a mixture of extracts from plants.

65.   Sckhoretskii, V. M., "Hardened Fuel for Creating Pyrotechnic
       Effects for Motion Pictures". Tekhn. Kini i Televideniya,
       Volume 6, No. 10, pp 63-6, 1962. C. A. $\underline{58}$, 3263$_c$ (1963).

       A formula is given and special apparatus is described for
       preparing fuel briquets for use in pyrotechnic displays.
       Kerosene or benzene is emulsified with a solution of casein
       and phenol-formaldehyde resin and hardened with oxalic
       acid and formaldehyde.

66.   Tamura, K., Japanese Patent 8-82 (to Meiji Confectionary, Ltd.),
       1957. C. A. $\underline{52}$, 11448$_c$ (1958).

       The procedure is described for treating an aluminum soap
       so as to render it capable of forming a stable gel with
       vegetable oil.

67.   Turk, W., Brenner, A., French Patent 836,341, (1939). C. A.
       $\underline{33}$, 5555$_4$ (1939).

       Benzene or gasoline may be brought to a gelatinous state by
       mixing with them a quantity of higher organic acids, more
       or less sulfonated, alone or mixed with a salt of that acid
       and at slightly raised temperature.

68.   Van Strien, R. E., Towle, P. H., U. S. Patent 2,751,283 (to Standard Oil Co.), 1956. C. A. <u>50</u>, 13483$_a$ (1956).

       Aluminum soaps are used as gelling agents for hydrocarbon liquids.

69.   Vaterroot, P., U. S. Patent 2,719,782 (to Botany Mills, Inc.), 1955. C. A. <u>50</u>, 3764$_f$ (1956).

       A solid gel is formed by the addition of 8 to 15 percent lanosterol to liquid hydrocarbons.

70.   Villa, E., U. S. Patent 2,801,910, (1957). C. A. <u>52</u>, 1602$_f$ (1958).

       Production of a high heat fuel gel is described. Procedure involves mixing of liquid fuel with a long chain paraffinic hydrocarbon or polymer thereof.

71.   Wheat, J. A., Mac Leod, D. A., Dunlop, R. G., Sheffer, H., "Preparation of Aluminum Octoate and Aluminum Isooctoate". <u>Can. J. Chem. Eng.</u>, Volume 38, pp 55-61, 1960. C. A. <u>54</u>, 14503$_g$ (1960).

       The aluminum soaps of 2-ethylhexanoic acid and isooctanoic acid have been prepared as hydrocarbon gelling agents.

72.   Woods, D. E., Taylor, A. J., "Preparation of Aluminum Soaps by a Continuous Process. III. Aluminum 2-ethylhexoate". <u>J. Appl. Chem.</u> (London), Volume 10, pp 197-9, 1960.

       A much stronger gel was obtained with aluminum 2-ethylhexoate than with aluminum laurate or nonanoate.

73.   Woods, D. E., Taylor, A. J., Lord, G. I., "The Production of Hydrocarbon Gels by Controlled Feeding of Compressed Aluminum Soap Cylinders into Heated Gasoline". <u>J. Inst. Petrol.</u>, Volume 48, pp 333-8, 1962.

       A pilot plant is described in which the compressed soap cylinders were fed at a uniform rate while being mechanically

disintegrated into a stream of heated gasoline to produce
15 to 20 gallons of gel/minute.

74.   Zhuze, T. P., "Gelation of Solutions of Normal Paraffins and of
        Paraffinic Petroleum Derivatives", Kolloid Zhur., Volume 12,
        pp 265-74, 1950.

        The apparatus and results of stress measurements are
        given for a paraffinic gel. The apparatus consisted of a
        plate slowly withdrawn from the gel with stress being
        determined as a function of deformation.

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13 ABSTRACT

Progress is reported on rapid methods for gelling aircraft fuels. The most promising systems consist of amines and diisocyanates. The properties of the gel are influenced by the structure of the amine and isocyanate. Various types of gels can be produced. These include particulate, viscoelastic, and dilatant gels. Gelation rates as fast as 0.04 second were obtained. In addition, several systems will rapidly gel fuel from -55°C to 60°C. The results show that the various gels will retard the burning rate of the fuels and will contain the fuel while burning. The viscoelastic and dilatant gels have excellent impact properties. The gelation of aircraft fuel will significantly decrease the fuel vaporization rate. A comparison was made of the various gels prepared. Some of the gels are almost as effective at 2.5 weight percent concentration as at a concentration of 4.0 weight percent.

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